

**THE MIGRATION OF LONG-LIVED
RADIOACTIVE PROCESSING WASTES
IN SELECTED ROCKS**

**Annual Report to the Office of Waste Handling
Project AN0115A
FY 1977**

by

**Sherman Fried, Arnold M. Friedman, Donald Cohen,
John J. Hines, and Richard G. Strickert**

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Chemistry Division

April 1978

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
INTRODUCTION	2
BEHAVIOR OF NEPTUNIUM WITH SPECIFIC ROCKS AND MINERALS	4
EXPERIMENTAL	5
RESULTS AND DISCUSSION	6
MIGRATION OF ACTINIDES FROM DISPOSAL SITES	11
EXPERIMENTAL	12
SORPTION OF TECHNETIUM AND IODINE ON ROCKS AND MINERALS	18
INTRODUCTION	18
EXPERIMENTAL PROCEDURES	19
RESULTS AND DISCUSSION	23
SUMMARY AND CONCLUSIONS	36
DISCUSSION	38
REFERENCES	41

LIST OF FIGURES

<u>Fig. No.</u>		<u>Page</u>
1	Changes in Absorption Spectrum of Np(V) with pH	7
2	Absorption Behavior of Np(V) on Los Alamos Tuff	9
3	Actinide Distribution at Disposal Site	13
4	Actinide Distribution in Laboratory Model	16
5	Vertical Distribution of Pu in CRNL Core	17
6	Schematic Diagram of Column Made with Los Alamos Tuff Rock Cylinder	20
7	$^{131}\text{I}^-$ on Saturated Los Alamos Tuff	24
8	$^{131}\text{I}^-$ on Limestone	25
9	$^{131}\text{I}^-$ on Chalcopyrite	26
10	$^{131}\text{IO}_3^-$ on Chalcopyrite	27
11	$^{131}\text{IO}_3^-$ on Bournonite	28
12	$^{95\text{m}}\text{TcO}_4^-$ on Limestone	30
13	$^{95\text{m}}\text{TcO}_4^-$ on Chalcopyrite	31
14	$^{95\text{m}}\text{TcO}_4^-$ on Bournonite	32

LIST OF TABLES

<u>Table No.</u>		<u>Page</u>
I	Molar Absorptivity ($l/mol\text{-cm}$) of Np(V) as a Function of pH . .	6
II	Solubility of Np(V) vs. pH	6
III	Sorption of Np(V) from Water	10
IV	Composition of Effluents	14
V	Radioisotopes Used in Experiments	19
V-A	Fraction Sorbed on Crushed Rock	29
V-B	Fraction Sorbed on Crushed Rock	33
VI	Fraction Sorbed on Mineral	34
VII	Fraction Sorbed on Chemical Compounds	34
VIII	Iodide Fraction Sorbed on Minerals	35

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ABSTRACT

Laboratory scale models have been constructed of the Pu-Am disposal areas at Los Alamos Scientific Laboratory and the migration of radionuclides determined. These results were compared to the migration at the actual disposal area as measured by analyzing core samples. It was observed that the laboratory model accounted for the extent and characteristics of the Pu migration quite well but did not describe as closely the features of the Am migration. This latter observation was probably due to the differences in the source terms. These results show that laboratory modelling is useful for site evaluation.

Vertical distributions of Pu from the Chalk River Nuclear Laboratory (CRNL) disposal site have been determined on cores of the sandy clay supplied by CRNL. This constitutes the first step in a similar laboratory-field model comparison in a different type of stratum and hydrological condition.

Iodine-129 and technetium-99, nuclides formed in the fission process, would exist as anions; I^- , IO_3^- , and TcO_4^- because of the oxidizing conditions in processing. It was found that the migration of these ions was very little retarded by rocks such as LASL tuff and Salem limestone. On the other hand, selected minerals containing copper and sulfur have been found to react strongly to remove these ions from solution and may be potential "getter" materials for the fixation of these ions.

A study of neptunium chemistry has shown that Np(IV) and Np(V) are the most likely oxidation states of this element to exist in ground water. While Np(IV) is easily immobilized because of its extreme insolubility, Np(V) does not bind strongly to many strata. However, it has been shown in this report that minerals containing calcium carbonate or phosphate remove Np(V) from solution in ground waters. Groundwater containing Fe(II) can reduce Np(V) to Np(IV) thus converting it to a relatively immobile species.

In the modeling experiments described with I^- , IO_3^- , and TcO_4^- ions as well as in our previous studies with Pu it has been frequently observed that the distribution of the radioactive materials does not correspond to the gaussian distribution predicted by an equilibrium chromatographic calculation. This can have an important effect on nuclide migration and the reasons for this behavior should be examined.

INTRODUCTION

The major aim in the migration study program carried out at Argonne National Laboratory is to determine the important migration characteristics and parameters of the long lived actinide and fission product nuclides in the lithosphere. This information is to be used as a basis for evaluation of the retention of these waste products at future repository sites.

The ultimate barrier to migration from a repository as well as the conduit to the environment will be the surrounding deep rock strata. It is implicit in this investigation that water moving through deep strata will be the sole effective mobilizing agent for the radionuclides from the point of original emplacement. This work has therefore been concerned with the behavior of various aqueous solutions of radionuclides in contact with selected minerals and rocks in various forms. Attempts are made to determine the binding or the " K_d " with respect to rocks and minerals as well as determining the extent of migration under various conditions. It is hoped to be able to relate these findings to radionuclide behavior under actual field conditions and extrapolate them to the future in such a manner that a credible safety assessment can be made.

The work carried out on radionuclide migration in geologic strata described in this report resulted largely from a conference held at ERDA, Germantown with members of the Division of Nuclear Fuel Cycle and Production in Jan. 1977. It was suggested that the behavior of neptunium(V), particularly that portion resulting from the decay of already mobilized ^{241}Am , was of sufficient concern to warrant immediate study. Additionally, the migration characteristics of the anionic technetium and iodine also required attention. The presence of the long lived ^{129}I and ^{99}Tc in process wastes must be taken into account in any deep burial isolation scheme. It was therefore agreed to examine the migration of these nuclides with a view to understanding their role in waste isolation and to find means of immobilizing them if it should prove necessary.

There is very little justification for laboratory studies of migration unless they can be seen to be applicable in the field. Thus another aspect of the work carried out in this laboratory is concerned with examining sites at which disposal of radionuclides has already taken place. Corings of some of the sites already available to us and analysis of the radionuclide content as a function of depth is a good measure of the actual behavior of a disposal site over the time interval of "operation".

The sites chosen for evaluation were the sites at Los Alamos and the Chalk River Nuclear Laboratory (CRNL). The disposal site in the former case was rock (Los Alamos tuff) exposed to weather and climate while the latter disposal site was in a sandy clay also so exposed.

This report contains sections on each of the aforementioned aspects of radionuclide migration. Experiments are also described to discern and delineate binding properties and parameters of various minerals and rock species for several nuclides.

In some cases batch experiments were run to obtain " K_d 's" of the rock or mineral with a particular nuclide. In others actual migration (or binding) with a solid sample of the rock was determined. One fact appears to emerge from the experiments: a simple equilibrium chromatographic model is not sufficient to explain the observed behavior of radionuclides interacting with real natural rocks.

It has also become apparent that the oxidation states of the radionu-

clides are important. This statement is not meant to be profound. It is, of course, obvious that the chemistry of the nuclides is important in an essentially chemical reaction with the rock strata. Nevertheless this truism is frequently ignored and the literature contains much work on radionuclides in the environment where the oxidation states and the role they play in migration is unknown or disregarded. Therefore it is felt that this aspect of the migration study should be explicitly stated.

The situation is complex. The various oxidation states of a given radionuclide may bind differently to a given strata and oxidizing or reducing components in the geologic material may react with the radionuclide to change its original oxidation state. It is also clear that the various oxidation states will have different reactions with complexing agents which may be present in the subterranean water(1,2). Because of these effects it is felt that it was important to determine the stability of the oxidation states of Pu and Np under conditions expected in the vicinity of a repository.

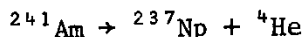
Techniques that have been developed in this program are presently being applied to collaborative research programs with Battelle Northwest and Sandia Laboratories. These collaborations are aimed at providing information on nuclide migration for safety evaluation programs at the proposed future Office of Waste Management (OWI) and Waste Isolation Pilot Plant (WIPP) facilities.

Finally it should be stated explicitly that most of the programs described in this report are empirical in their approach. It is understood that fundamental research in this field is desirable but the exigencies of the task of evaluating a prospective repository require a direct "engineering approach". When basic information is required to understand the empirical observations, the appropriate studies should be undertaken.

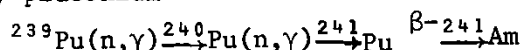
BEHAVIOR OF NEPTUNIUM WITH SPECIFIC ROCKS AND MINERALS

The work reported in this section is still in progress but since interest was evinced in neptunium migration because of its biological activity (1) and the fact that it will ultimately become the most abundant alpha emitting nuclide (2) it was decided to present the material here as an interim progress report.

Neptunium-237, an α -emitting actinide ($T_{1/2} = 2.2 \times 10^6$ y) is generated by nuclear reactions during reactor operations and is found in spent reactor fuel*. It may appear in reprocessing wastes according to the particular process used. This nuclide also results from the decay of americium-241 according to the equation



Americium-241 in turn is produced during reactor operation by second order capture of neutrons by plutonium



It is this latter source of Np that is important in the waste isolation context since it has been reported (3) that Am migrates much faster than Pu(IV) does in certain geologic strata. Thus neptunium may be formed as a decay product of Am at some distance from the original repository. On the other hand, the "in situ" Np formed by direct nuclear reaction within the fuel as mentioned above is probably in the easily hydrolyzed insoluble (IV) state and would not migrate easily. This may be inferred from the fact that the Np will be incorporated in some kind of glass and it is likely that the melting of the glass at $\sim 1000^\circ\text{C}$ will decompose any higher oxidation states. If this neptunium, however, should actually reside in the waste in higher oxidation states it may migrate much more readily and the problem could become more acute.

The Np(V) oxidation state is stable and soluble (4) over a wide range of pH's including the pH of natural ground water which varies from approximately 4 to 9. It is in this region of pH exhibited by ground water that a study of Np chemistry and the reactions with various minerals and rocks has been made.

* The specific activity of the alpha emitting ^{237}Np is 1.58×10^2 disintegration/minute/microgram.

This report is divided into two parts. The first part concerns itself with the probable oxidation state of neptunium in radioactive waste solutions and the second part with the effect of certain geologic materials on solutions of neptunium.

EXPERIMENTAL

Neptunium-237 obtained from Oak Ridge National Laboratory was precipitated from solution as a hydroxide by addition of NH_4OH . The soluble cations remained in the supernatant. After washing with water the purified precipitate was used as stock for further preparations.

To prepare Np(V) the Np hydroxide was dissolved in 0.1 N HCl and converted to Np(VI) by passing ozone through the solution. When the reaction was complete, the Np(VI) was converted to Np(V) by addition of NaNO_2 which quantitatively reduces Np(VI) . Ammonium hydroxide was added to precipitate the Np(V) hydroxide which was then washed repeatedly with water. Np(V) hydroxide was dissolved in dilute HCl and the pH adjusted to 7 or other values by adding LiOH . This solution was then used as the stock solution for the migration and sorption experiments.

The geologic materials used in these experiments were either very common substances, such as sandstone, basalt, tuff, shale and limestone or else minerals such as galena, chalcopyrite and apatite, which had been already tested with the environmentally important anions I^- and TcO_4^- (5).

The sorption of Np(V) on Los Alamos tuff or Salem limestone was studied using an elution method similar to that employed in the plutonium-ameridium migration study (3). A sample of Np(V) in about 50-100 λ of solution ($\text{pH} \approx 7$) (about 40 μg) was placed on the surface of a small cylinder of the rock and dried. Water, previously contacted with the appropriate powdered rock for 1 week was passed through the rock to elute the neptunium. The Np in the eluate was measured by α -counting the dried residue on a stainless steel plate.

Batch experiments were carried out in spectrophotometer absorption cells. The granulated or powdered mineral or rock, 250 mg and 2 ml of the neptunium solution were placed in a cell and the absorption spectrum measured at 980 nm (the absorption peak of Np(V)). The cell was mechanically agitated for various lengths of time, centrifuged and the absorption spectrum re-measured. In some cases α -counting was also used for analysis.

RESULTS AND DISCUSSION

Neptunium exhibits five oxidation states in aqueous solution: 3, 4, 5, 6 and 7. However, Np(III) is very easily oxidized and Np(VII) very easily reduced. Consequently, these two oxidation states are probably not important in the context of waste isolation. Neptunium(IV) is easily hydrolyzed and quite insoluble in water at the pH of interest and Np(VI) has been shown to decompose slowly to Np(V) (6). It would appear therefore that initially at least, the behavior of Np(V) should be the primary objective of investigation in migration studies.

The absorption spectrum of Np(V) in aqueous solution exhibits a prominent peak at 980 nm which lends itself admirably for analytical purposes. Table I shows the molar absorptivity of Np(V) as a function of pH. These data indicate that the same species of Np(V) is stable from the acid region up to a pH of about 8.7. Beyond this pH the 980 nm peak of Np(V) changes; first a shoulder and then a new peak at 990 nm appear and finally at a pH of 14 the main Np(V) absorption peak has shifted to 1010 nm. The successive changes are shown in Figure 1. The change in spectra indicate that new Np(V) species are formed.

The solubility of Np(V) in water as a function of pH is given in Table II. Its solubility in the pH region 4-7 is greater than 0.01 M or more than 2 mg/ml. The data in Table II were obtained by assaying the neptunium solution at each pH.

Table I. Molar Absorptivity (l/mol-cm) of Np(V) as a Function of pH.

Peak (nm)	pH = 1.2	2.7	4.6	7.4	8.4	8.7	8.8	9.2
1116	6.6	5.9	6.1	6.7	5.3			
1096	27	26	26	26	24		20	
1024	9.6	9	8.8	10	11			
980		420			387	410	271	192
616	25		23	26		30		

Table II. Solubility of Np(V) vs. pH.

pH	Np(V) (moles/liter)
4.6	.0176
7.4	.0118
8.4	.00075
8.8	.00055

Aqueous solutions of Np(V) are stable to either oxidation or reduction by H₂O. They are also evidently stable to the action of radiolysis products; at a pH of 6.1 a solution exposed to 1×10^6 rad from a ⁶⁰Co source showed no change in oxidation state.

It has been mentioned that Np(IV) is easily hydrolyzed in water and that the products are very insoluble. It has been found that air will oxidize these hydrolyzed species in water to the soluble Np(V). The growth of the 980 nm peak of Np(V) can easily be seen when air is in contact with Np(IV)

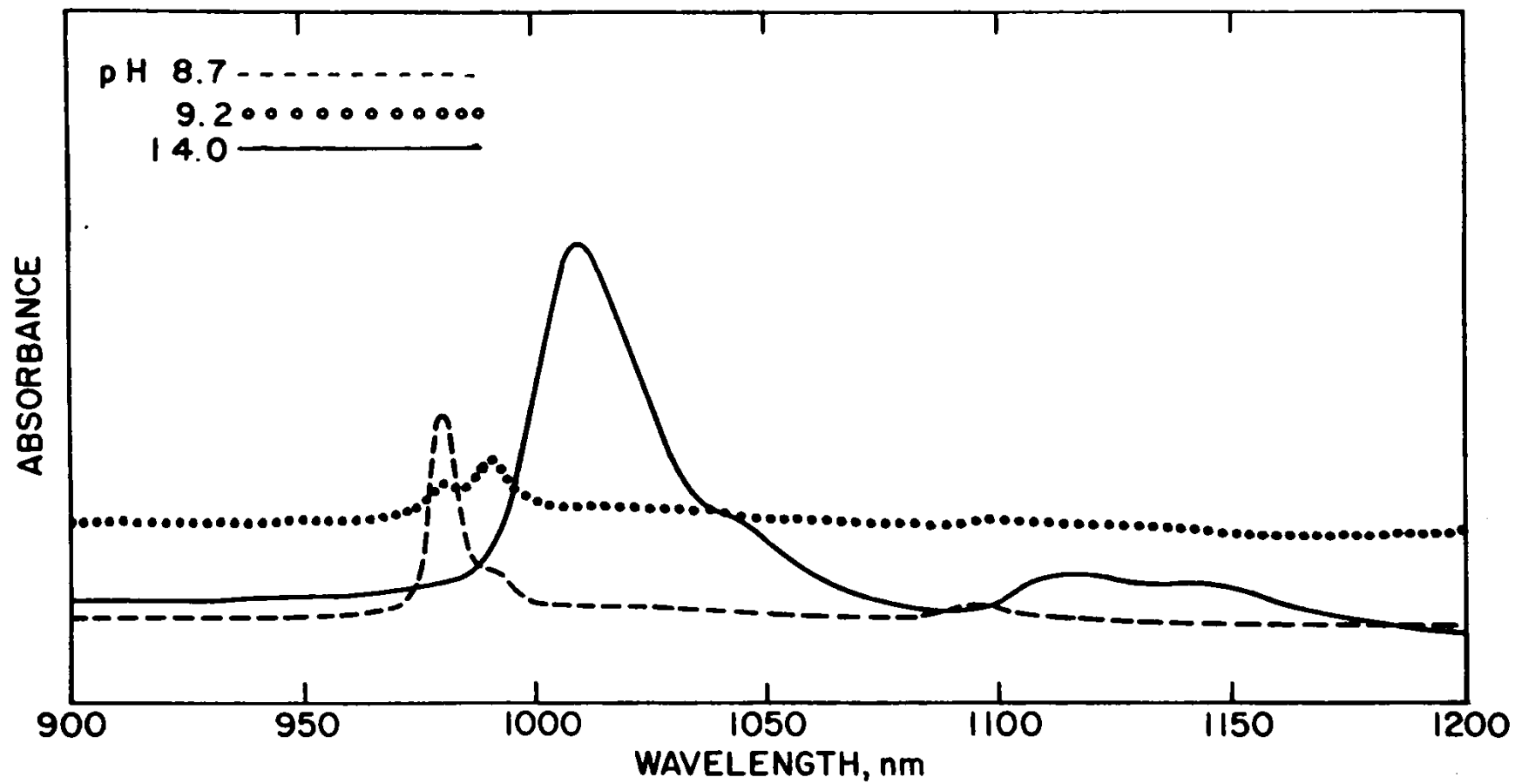


Fig. 1. Changes in Absorption Spectrum of Np(V) with pH

solids in water.

It was observed in this investigation that Fe(II) in solution at pH 5-7 will slowly reduce Np(V) to Np(IV). Thus the oxidation state of neptunium will depend upon the presence of air or Fe(II) solutions. In the presence of atmospheric concentrations of oxygen the iron will be Fe(III) and no reduction of Np(V) to Np(IV) can be expected. In deep rock strata where the ground water generally contains Fe(II) it can be expected that Np will be in the IV state if no other oxidizing agents are present while, in regions much closer to the surface where the water may contain oxygen, Np(V) will probably be the dominant species. This effect, of course, has implications for the reactions of Np in rock strata with consequent effects on its migration, and is also being investigated for Pu.

Several experiments were performed to measure the retention of Np(V) on tuff (Los Alamos tuff; consolidated volcanic ash) similar to the Pu studies (3). Three separate experiments showed that Np(V) is not appreciably adsorbed by tuff and is eluted within a few free column volumes. The data for one of these experiments are shown in Figure 2. The sharp peak in the elution curve occurs at less than two free column volumes (a free column volume is defined as the porosity of the rock times its geometric volume and is determined by first weighing the rock dry and then saturated with water).

Because of the stability of Np(V), its solubility and its possibility in ground water, it is important to find common minerals or rocks capable of immobilizing it. In order to perform a rapid survey of mineral types it was decided to look for indications of absorption of Np(V).

It should be emphasized that these experiments were not aimed at measuring exact values of K_d and in general were only run for a few hours and not to equilibrium. It is proposed for future work to select the most promising minerals and measure sorption as a function of temperature, pH, concentration of Np and mineral particle size as parameters affecting the equilibrium.

Thus a series of batch experiments were made at room temperature in which 2 ml of Np(V) stock solution (10^{-4} M at pH \approx 7) was mixed with 0.25 grams of the various solids directly in a spectrophotometer absorption cell. The 980 nm absorption peak of Np(V) was monitored after various times of mixing.

For limestone, granite, and shale the 980 nm peak was split into two peaks. This indicated that the solutions had a pH of about 9 and indeed the pH measurement did show these three solutions to have pH's from 8.7 to 9.7. The surprisingly high pH of granite-equilibrated water can be accounted for by the presence of ammonia in the granite. This has been demonstrated by the experiments by Rayleigh (7).

While the 980 nm peak only monitors the Np(V) in solution and there could have been reduction to insoluble Np(IV) or oxidation to Np(VI) it was felt that the Np(VI) spectrum would have been observed and any substantial amount of Np(IV) would have precipitated at this pH.

Except for the siderite experiment there was no appreciable amount of reducing agent in those minerals that absorbed the Np(V). The other reducing minerals chalcopyrite, galena, and pyrite did not remove Np(V) from solution. However, since this study does not include other mineral samples or even a range of surface areas it cannot be said that reduction to Np(IV) will not be important. On the contrary as has already been pointed out Fe(II) in solution is capable of reducing Np(V). It may be possible to have a heterogeneous reaction at a solid surface and the reaction of Np(V) with

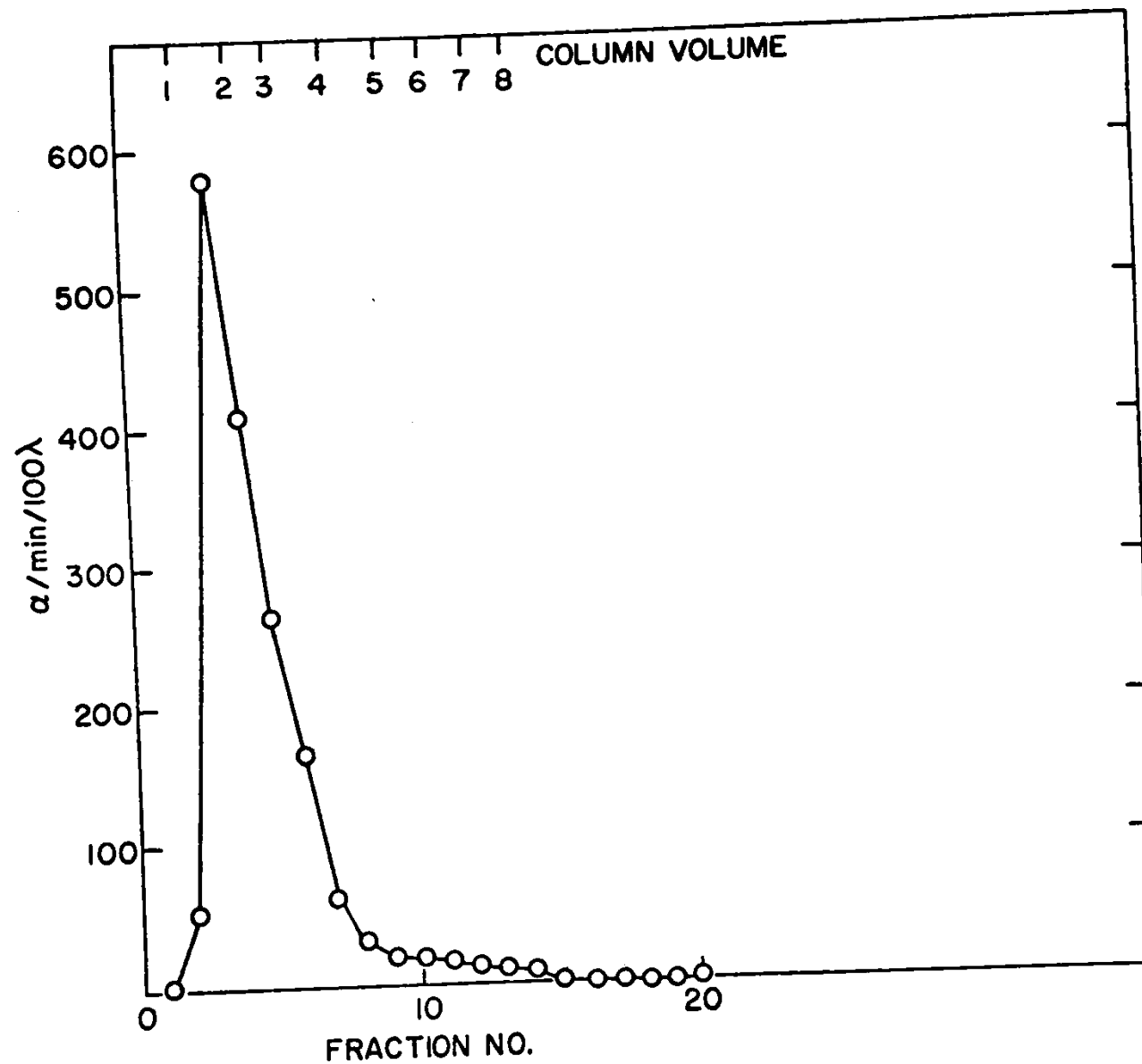


Fig. 2. Absorption Behavior of Np(V) on Los Alamos Tuff

siderite (FeCO_3) is being investigated*.

Table III shows the results of these experiments. The materials in group A showed no sorption; group B small sorption, and group C substantial sorption. Thus there are materials found in geologic strata that have the potential to immobilize Np(V).

After observation of the absorption by limestone in the previous experiment, a macro experiment with a 9 gram piece of Salem limestone was carried out. Thirty-two micrograms of Np(V) at a pH of 6 in 100 λ of solution were deposited on the surface of a cylinder of limestone 2 cm in diameter and 1.1 cm thick. The limestone was then air dried. A head of 1.2 meters of water was sufficient to move pre-equilibrated water through the rock at a reasonable rate, 10 to 15 ml./day (100 meters/year). The water was pre-equilibrated with powdered limestone and had a pH of 9.1.

Table III. Sorption of Np(V) From Water.

Absorbent		pH	Time (hours)	%Np(V) Remaining in Solution
A.	Chalcopyrite CuFeS_2	7 \pm .5	3	100
	Galena PbS	7 \pm .5	1	100
	Pyrite FeS_2	7 \pm .5	2	100
B.	Magnetite Fe_3O_4	7 \pm .5	2	74
	Basalt Silicates	7 \pm .5	1	77
C.	Apatite $\text{Ca}_4(\text{CaF})(\text{PO}_4)_3$	7 \pm .5	2	1
	Azurite $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	7 \pm .5	2	3
	Sandstone Silicates	7 \pm .5	3	54
	Shale Silicates	\sim 9 \pm .5	3	40
	Siderite FeCO_3	7 \pm .5	1.5	14
	Limestone CaCO_3	9 \pm .5	2.5	14
	Granite $\text{SiO}_2, \text{KAlSi}_3\text{O}_8, \text{CaAlSi}_3\text{O}_8$	9 \pm .5	4.0	17

Samples of the eluate were collected at time intervals from six to 72 hours and 4.5 to 44 ml. in volume. Each sample was evaporated nearly to dryness and the entire sample was plated and alpha counted for neptunium. Initially 25,700 α /min of neptunium were placed on the limestone and after 1178 free column volumes a total of 130 α /min were eluted, or approximately 0.5% of the original deposit. After the experiment was completed it was determined that the bulk of the Np was absorbed in the piece of limestone. This was accomplished by counting the \sim 300 keV γ -ray of the ^{233}Pa daughter after equilibrium with the ^{237}Np . This method enabled the determination of ^{237}Np without tedious chemical manipulations. Thus limestone does absorb and bind Np(V) ions. This result is in agreement with the data in Table III.

*The source of the minerals is as follows: chalcopyrite, Ontario; galena, Illinois; pyrite, Nevada, Colorado; magnetite, Burnier, Brazil; basalt, Columbia River; apatite, Renfrew, Ontario; azurite, Blue Ball Mine, Gila County, Arizona; sandstone, Ohio barrier; shale, Pierre Front Range Precast Concrete Company; Shale Point Boulder Colorado; siderite, Arksukfjord, Greenland; limestone, Salem, Bedford Indiana; granite, Nevada Test Site, Nevada.

MIGRATION OF ACTINIDES FROM DISPOSAL SITES

The adsorption studies and modeling experiments carried out at this laboratory are complimented by a program of radiometric analysis for actinide elements of core samples from existing waste disposal sites. Samples have been obtained from two such sites; the Los Alamos Scientific Laboratory (LASL) and the Chalk River Nuclear Laboratory (CRNL). Neither site can be considered an ideal model for deep geologic disposal, however they are the best available for study at this time. In each case large volumes of waste process solutions and CRNL solid waste as well, were disposed of in shallow backfilled trenches and left exposed to the weather. At the LASL site these conditions were arid but the CRNL site drained into a swamp. The matrix through which the waste at LASL percolated was tuff, a compacted volcanic ash, the CRNL matrix was a sand-clay mixture. Each site has been inactive for at least ten years but adequate records have been maintained as to time, amount and nature of discharges (8,9).

EXPERIMENTAL

The nature of the sites required diverse procedures for analysis. The actinide elements at the LASL site were contained in a small area because of the high adsorptive properties of the matrix and the arid conditions. Core samples were taken at six inch intervals from below the floor of a disposal trench to a depth of twenty feet. The floor being six feet below the surface of the ground. While in use $\sim 2 \times 10^7$ gallons of waste containing 100-1000 pCi of plutonium per milliliter were discharged between 1945 and 1967. The area has since been backfilled and regraded. A portion of each core was dried and ground prior to sample preparation. A weighed aliquot of each was then compacted into 2 mm x 15.9 mm disks contained in a cardboard holder. The concentration of ^{239}Pu and ^{241}Am in each sample was determined by low energy photon spectroscopy (LEPS) using a 2 cm² by 0.5 cm thick planar lithium drifted germanium detector in a large 6 inch thick steel shield.

This technique was employed in preference to the more conventional wet chemical analysis for several reasons. It eliminates uncertainties in sample preparation and handling. There are no reagent blanks, no question of sample dissolution or chemical yield. Furthermore less time is required for each analysis. In practice, each sample was counted for 15-24 hours and the resulting data manipulated by an on-line, real time computer system. Data handling consisted of subtraction of a normalized background, integration of the 60 keV gamma line to determine the ^{241}Am content followed by stripping the Am from the combined spectrum with a normalized ^{241}Am library standard spectrum. Results were then calculated on the basis of pCi/g of dry sample. A plot of these results as a function of depth is shown in Fig. (3). Inspection of these data reveal several interesting characteristics. In spite of the large volume of discharge waste and over 20 years of rainfall, half of the actinides were retained within the top foot of the surface; less than 1% being found at depths greater than 14 feet and nothing below 20 feet. The geology and climate of the LASL disposal site are such that it is reasonable for discharges of tens of thousands of gallons not to penetrate greater than 20 feet. Evaporation is known to be the sole source of precipitation loss under such conditions and ground water recharge is not possible. It is safe to assume the same is true of waste discharges of such magnitudes. The plutonium shows the same behavior experienced in laboratory models of strong surface adsorption; forerunning exponential plume out to a small component at the leading edge. The Am data present a more complex picture.

The americium comes from two sources; the original process waste solution, and the continuous beta decay of its 13.2 year ^{241}Pu parent. It is this second source which generates Am long after disposal and at a depth dependent upon the migration of the precursor.

What is obvious, however, is that the majority of the Am migrated to a depth of 9 feet. In order to evaluate these results and to validate the laboratory modeling program, a scale model LASL disposal site was constructed. Synthetic process waste solutions spiked with ^{237}Pu and ^{241}Am tracers were prepared. The concentration and volumes of these solutions (see Table IV) were scaled according to the LASL records and percolated through a specimen of Los Alamos tuff, obtained from the site of the actual disposal trench. These solutions were introduced in sequence at a controlled flow rate of 65 meters per year with a metering pump followed by water equivalent to 20 years of rainfall. The specimen was then dried, sectioned and the actinide content of each section determined by gamma ray spectroscopy. A

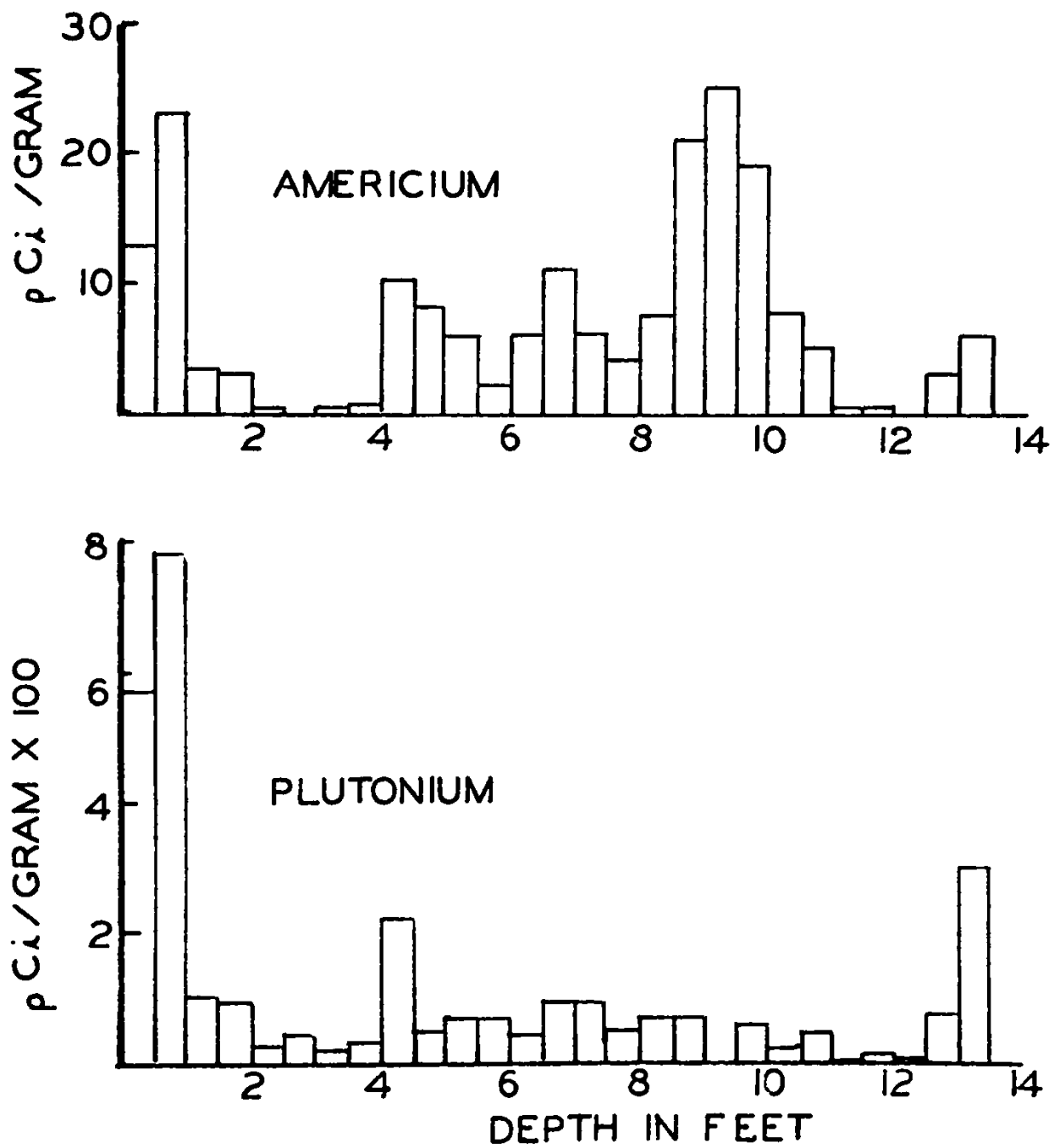


Fig. 3. Actinide Distribution at Disposal Site

Table IV. Composition of Effluents

Date	Volume (gallons)	Chemical Composition	Plutonium Concentration	Total Plutonium
1945 - 1950	1.4×10^7	160 ppm F^- 13 ppm NH_4^+	60 c/m/ml	45 g.
1951 - 1952	1.0×10^4	"Conc" ammonium citrate 200 ppm F^-	7×10^3 c/m/ml	3.7 g.
1953 - 1967	4.0×10^6	0.1 M $NaNO_3$	Trace	< 10 g.

plot (scale 1 cm = 2 ft) of these data is shown in Fig. (4). The plutonium results agree remarkably well with core samples; the same strong absorption near the surface with a plume to the leading edge. The depth of migration also agrees when the scaling factor is considered. The americium results are not as well correlated, but they do show greater migration for the bulk of the Am as compared to Pu. The lack of correlation may be due to the uncertainties in the Am source term.

The second site studied in this project (CRNL) presented a different set of problems. In 1954, 1500 gallons of a nitric acid waste solution containing 230 Curies of mixed fission products activity were poured into a shallow hole in the "A" disposal area of CRNL disposal site. This solution also contained 1-2 grams of plutonium. This site is a sandy swamp and the discharge was into an aquifer. The CRNL personnel have extensively studied this disposal site for migration of fission products as well as its geology and hydrology (10). Our contribution will be to determine the migration of Pu. Analytical measurements of Pu in cores from this site are complicated by the nature of the site; the small amount of Pu discharged, its dispersion by a large volume of water and the excess of gamma emitting fission products. Because of these conditions, the non-destructive instrumental method employed with LASL samples was found not practical. Much effort was expended developing the simple yet effective radiochemical procedure required. Each sample was dried and ground to a fine powder. One or two gram aliquots in polyethylene centrifuge tubes were leached overnight in 10 ml of 8 N HNO₃ with gentle end over end tumbling. Tests on synthetic and calibrated standard samples indicate the leaching step quantitatively removes Pu from the sand. Samples were then centrifuged and the acid withdrawn and contacted with 2 ml of a 30% solution of Aliquat 336 (a liquid quaternary amine ion exchanger) in xylene. Extraction was followed by scrubbing with 4 M HNO₃ and 9 M HCl primarily to remove Th, the only significantly interfering element. Pu was then back extracted into 1 M H₂SO₄, neutralized to pH 2 with NH₄OH and electroplated onto platinum disks for alpha pulse height analysis. Excellent quality plates were obtained resulting in well resolved spectra. Results were normalized after yield corrections to pCi/g of dry sample. Thus far one set of samples from a single core has been processed representing a vertical cross section of Pu at a coordinate near the fenced in disposal site, approximately 65 ft from the original discharge. Figure (5) is a plot of these data. Obviously little can be inferred from only one coring but numerous archival samples are available and the fullest cooperation of CRNL has been assured in supplying those and/or any additional cores required. The goal is to measure the extent of the Pu migration as well as calculate relative migration coefficients from horizontal distance migrated as compared to known water flow rate in this medium.

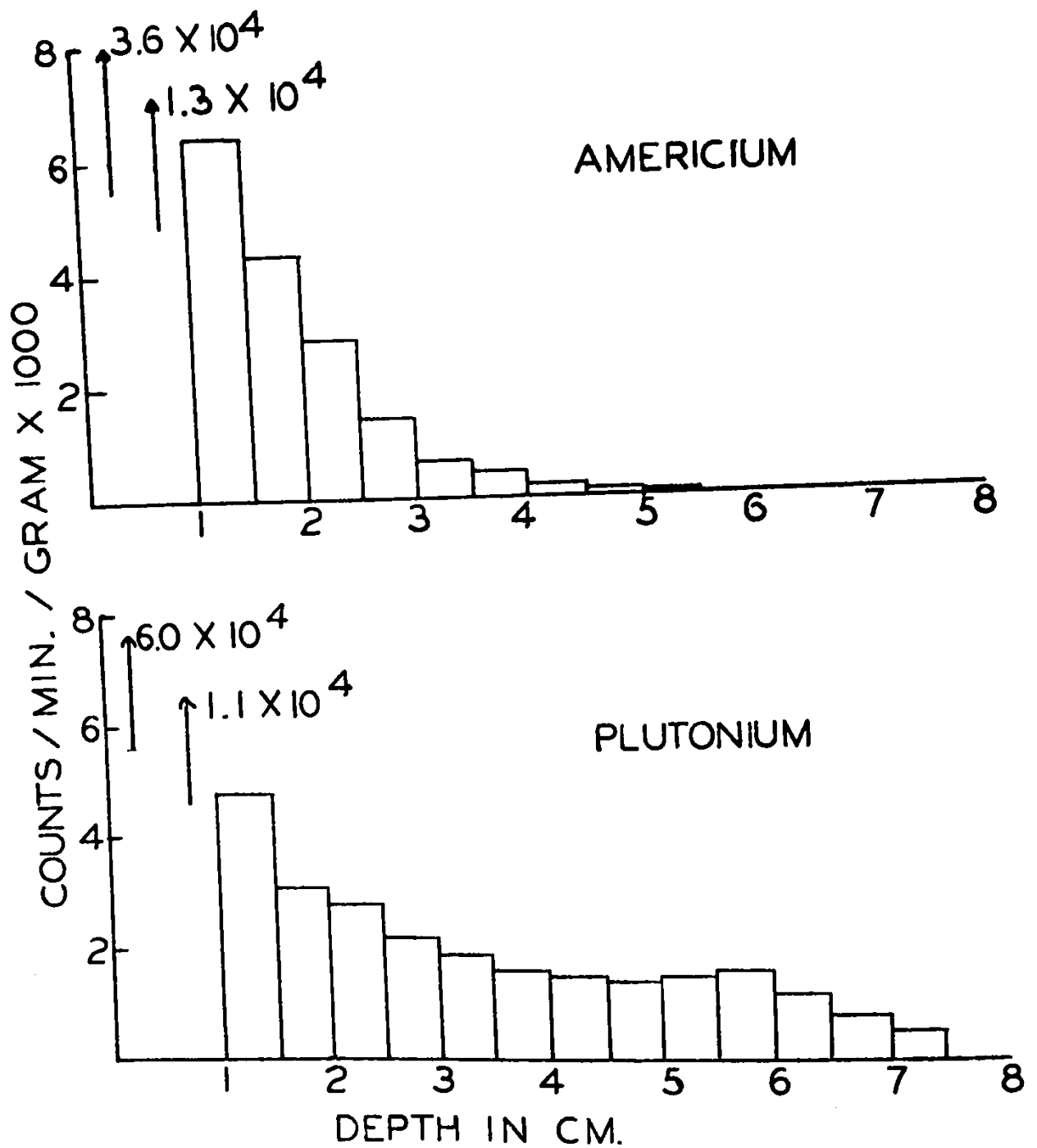


Fig. 4. Actinide Distribution in Laboratory Model

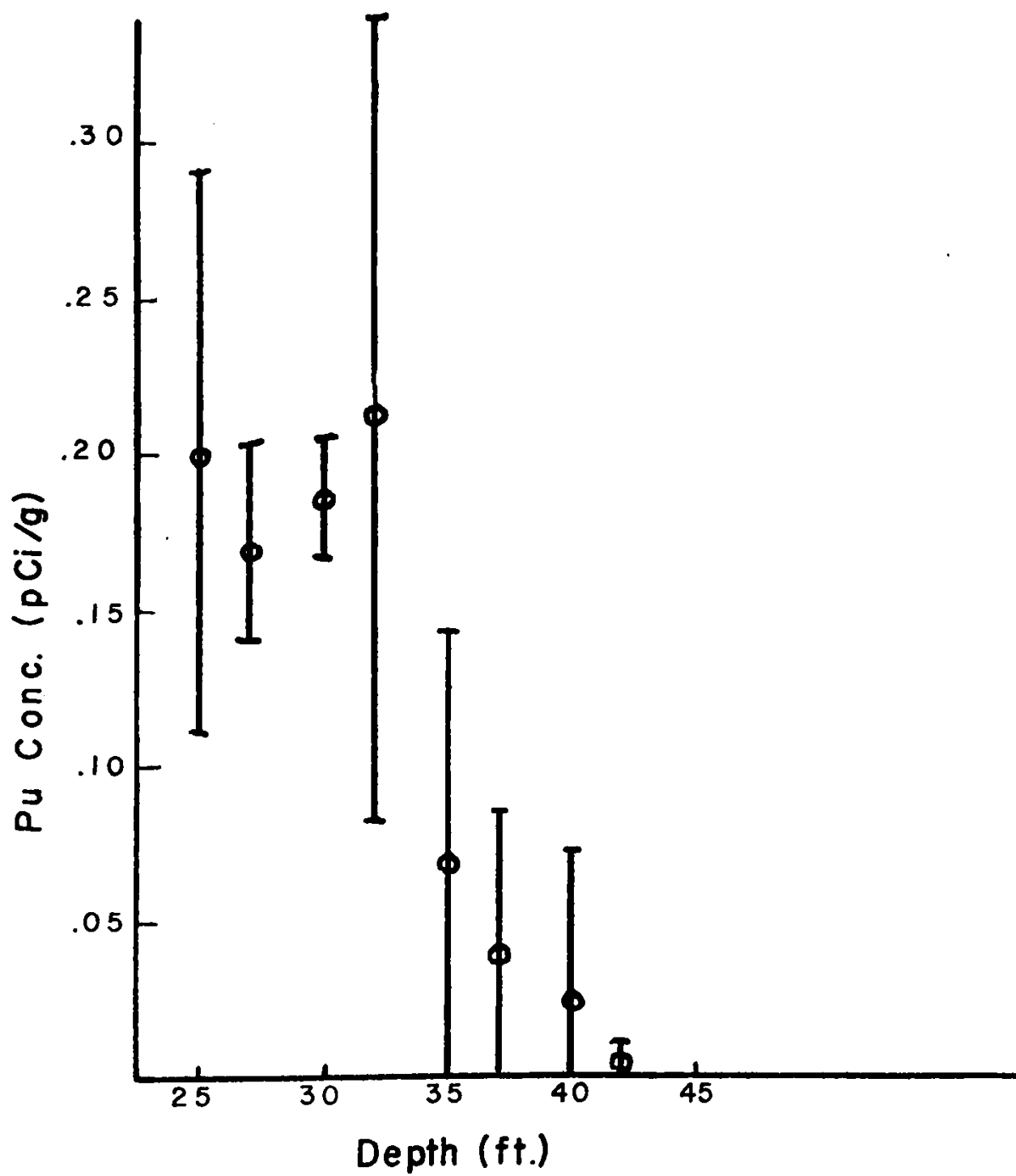


Fig. 5. Vertical Distribution of Pu in CRNL Core

SORPTION OF TECHNETIUM AND IODINE ON ROCKS AND MINERALSINTRODUCTION

Most radioactive isotopes whose half-lives are long enough to require deep geologic waste disposal are cationic. Known ion-exchange and other absorption processes within the rock strata substantially slow the migration of these radioactive cations in solution (3,11-17). For example, it has been shown recently (3) that the relative migration coefficient for plutonium in various rock types is approximately 100 micrometers per meter of water flow (i.e., the plutonium in the groundwater will advance 100,000 times more slowly than the groundwater front).

Stable chemical forms of technetium and iodine, however, exist as anions in groundwater solutions. Many soils and lithic strata do not bind anionic species (15,16). In fact, for these anionic species no significant delay in migration due to ion-exchange processes in common silicate-bearing rocks (e.g., tuff, basalt, granite) has been noted (5). Technetium and iodine, moreover, have long-lived isotopes present in nuclear wastes which may pose an environmental hazard ($T_{1/2}$ for $^{99}\text{Tc} = 2.1 \times 10^5 \text{y}$, $T_{1/2}$ for $^{129}\text{I} = 1.6 \times 10^7 \text{y}$).

Because of these factors several sets of experiments have been carried out to examine sorption mechanisms other than ion-exchange which can immobilize the common anionic forms of technetium and iodine. The anionic species of interest are presumed to be:

- (1) pertechnetate (TcO_4^-)
- (2) iodide (I^-)
- (3) iodate (IO_3^-)

One possible sorption mechanism is the chemical reduction of the ions to a more easily immobilized form. Another possibility is the formation of an insoluble species by incorporation into the crystal lattice of an insoluble matrix (18).

To investigate these alternatives measurements were carried out on the absorption of pertechnetate, iodide, and iodate ions from a solution by various common minerals including those which may contain potential reducing or coprecipitating components. From the consideration of the chemistry of technetium and iodine it was expected that such "components" would contain copper, lead and/or sulfur. Included in this investigation were certain particular rock types which had already been used for small-scale radioactive waste disposal. Trenches cut in the local tuff at Los Alamos Scientific Laboratory had been used in the late 1940's and 1950's for liquid radioactive wastes. Some nuclear waste disposal had occurred in the basalt at the Experimental Breeder Reactor II near Idaho Falls, Idaho. Rock samples from the area around the Nevada Nuclear Test Site were also included.

EXPERIMENTAL PROCEDURES

A. Radiotracers

The radioactive isotopes used in these experiments were iodine-131 and technetium-95m chosen for their easily resolved gamma rays even in the presence of one another (Table V). Iodine-131 as iodide was purchased in car-

Table V. Radioisotopes Used in Experiments.

Isotope	Half-Life	Principal Gamma Ray Energy
^{131}I	8.04 days	364 keV
$^{95\text{m}}\text{Tc}$	60 days	204 keV

rier-free solution and diluted to convenient tracer levels. The iodate tracer was made by oxidation of iodide tracer with sodium hypochlorite, Chloramine B, or ozone (19). Technetium-95m was made at the Argonne cyclotron by the $^{93}\text{Nb}(\alpha, 2n)^{95\text{m}}\text{Tc}$ reaction. The niobium foil was dissolved in a solution containing 15 M HNO_3 and 28 M HF . The technetium was separated and purified by standard ion-exchange radiochemical techniques (20). The final tracer solution consisted of $^{95\text{m}}\text{TcO}_4^-$ in a dilute ammonium hydroxide solution.

B. Rock Cores (Tuff)

Initially, a series of experiments was carried out using small cylinders (3 cm x 2 cm diameter) of Los Alamos tuff, which is well suited for laboratory experimentation and has been used in migration studies of actinides (3,5). The outer surface was waxed and the rock cylinder was attached to a glass tube. Fifty microliters of iodide or iodate ion tracer were applied to the top of the dry tuff column; and water, previously equilibrated with crushed tuff rock, was dropped onto the column (Figure 6). The flow rate corresponded to a water front velocity of approximately 0.8 kilometer/year, a value in the range of measured aquifers (21). The water dripping from the porous rock was collected in vials, which were analyzed for gamma activity using a NaI scintillation counter. Experiments were also conducted in which the tuff cylinder was first saturated with water pre-equilibrated with crushed tuff rock before the radiotracer was applied.

C. Crushed Rock Columns

In other experiments, quantities (several grams) of crushed rock (60-100 mesh) were loaded into polyethylene or glass tubes, such as would be used for ion-exchange columns, and saturated with pre-equilibrated water. Approximately 30 microliters each of the pertechnetate tracer and iodide or iodate tracer were applied to the top of the saturated crushed rock column. Water, pre-equilibrated with the particular rock type, was passed through the column at a fixed rate. The equivalent water front velocity in these columns was approximately 1 kilometer/year or faster (and in some cases, discussed below, the water front velocity was considerably faster).

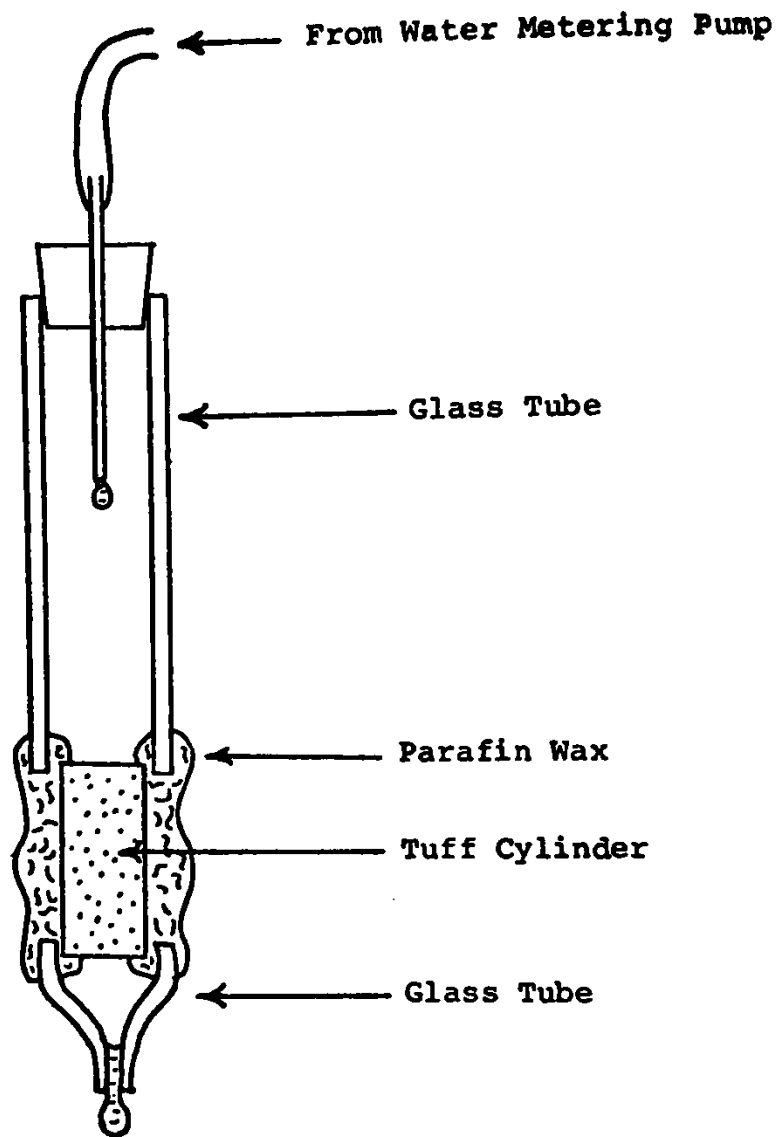


Fig. 6. Schematic Diagram of Column Made with Los Alamos Tuff Rock Cylinder

D. Batch Experiments

A method was devised to examine a large number of mineral samples to determine their relative ability to bind the pertechnetate, iodide, and iodate tracer. A weighed amount (~ 0.3 gram) of crushed rock or mineral (60-100 mesh) was added to a polyethylene vial along with 1 milliliter of water pre-equilibrated with the mineral. Measured amounts (approximately 5×10^5 dpm) of the pertechnetate tracer, and one of the iodine tracers were added to each vial. These vials were shaken continuously for periods of up to three days. After shaking, the vials were centrifuged and an aliquot of solution was removed from each vial and analyzed for activity to determine the amount of activity retained on the rock for each tracer.

A second series of experiments was designed to test the effects of using different pre-equilibrated solutions. A weighed amount of mineral was added either to one milliliter of its own pre-equilibrated solution or to one milliliter of pre-equilibrated solution of a different mineral. Tracers were added and the vials were shaken up to 5 hours. Afterwards, an aliquot of the solution was taken and the amount of tracer absorbed on each mineral were determined.

Batch experiments was carried out using weighed amounts of various chemical reagents in crystalline or powdered form. The procedure used was the same as in batch experiments with crushed rock. Water, pre-equilibrated with each chemical reagent, was added to a vial containing a weighed amount of the chemical. The vials were shaken for approximately three days, then centrifuged, after which an aliquot of solution was removed from each vial for measurement.

To measure the capability of the crushed rock columns to absorb macroscopic amounts of the iodide ion, a preliminary batch experiment was done in which non-radioactive ("carrier") iodide was added to the iodide tracer solution. This solution was then dispensed to the vials containing crushed rock and pre-equilibrated water. The amount of carrier was ~ 2 mg iodide ion per vial. Vials were shaken for approximately three days before the fraction of iodide absorbed by the crushed rock was determined.

E. Counting Procedures and Data Processing

In most of the experiments, the activity in the vials was measured on a Beckman Biogamma 3-Channel Gamma Spectrometer. The Biogamma uses a 3 x 3 inch NaI crystal scintillation detector. Two channels were used as windows for the 204 keV gamma ray of ^{95m}Tc and the 364 keV gamma ray of ^{131}I . The Biogamma includes a sample changer for up to 200 vials with automatic print-out of data for each vial counted. In some early experiments, a two-channel gamma spectrometer system was used with a two-inch NaI well crystal. This counter did not contain an automated sample changer and data was recorded manually.

In experiments using mixed tracers, separate iodine and technetium standards were used to determine the overlap of each tracer in the adjacent window. Correction for the overlap was made and the net activity due to each tracer in its respective window was determined.

1. Column Experiments - the total amount of activity applied to each column was determined by measuring aliquots of standard tracer solution. The tracer activity for each vial in a column series (corrected for background and any overlap) was then converted to the fraction of applied activ-

ity. The free column volume* for each experiment was estimated by measuring the weight difference in a measured geometric volume between dry and saturated columns†. Water flow rates were determined by timed measurements or by the rate set on a metering pump supplying pre-equilibrated water to the column.

2. Batch Experiments - The tracer activity (corrected for background and any overlap) was determined (as described above) for each vial containing an individual aliquot of solution. The fraction of activity (F_R) sorbed by the rock or chemical material was determined by Equation (1).

$$F_R = 1 - \frac{A_a}{A_T} \cdot \frac{V_T}{V_a} \quad (1)$$

where A_a = activity of the aliquot removed from the vial

A_T = total activity put into the vial

V_T = total volume of solution in the vial

V_a = volume of aliquot removed from the vial.

The total activity was determined by counting an aliquot of tracer solution in the same geometry. The volume V_a , was approximately one-half of V_T .

All vials in a given experiment were counted as a group within a few hours of each other. Therefore, no correction for radioactive decay of the tracers was included.

*A free column volume is defined as the total volume of the rock times the porosity of the rock.

†Tuff rock cores were saturated by placing the core in a beaker of pre-equilibrated water inside a desiccator and evacuating the air. Crushed rock columns were saturated by running pre-equilibrated water through the columns.

RESULTS AND DISCUSSION

A. Los Alamos Tuff Experiments

From the Biogamma counting data, the fraction of applied activity collected in each vial of measured volume was calculated as a function of the total amount of water collected. The total fraction of applied activity passing through the core was determined by summing up the activity in all the collection vials. In the Los Alamos tuff core experiments, using iodide tracer, over 90% of the activity passed through the tuff core. Most of the activity came through in the first few free column volumes. In the case of a saturated rock core (as shown in Figure 7), the peak of activity occurred after the initial column volume of water present in the rock core had passed through. In two free column volumes essentially all of the activity had come through the core. The results of using IO_3^- ion tracer on a tuff column (either saturated or dry) were similar to those using I^- ion tracer.

It is evident from the elutions of these tuff columns that (1) no significant amounts of iodine are being bound by the tuff, and (2) there is no significant delay in the migration rate of iodine (relative to that of the groundwater flow).

B. Crushed Rock Columns

When a crushed limestone column was used, 62% of the applied I^- activity came through, mostly in the first three column volumes (Figure 8). In contrast, when I^- activity was applied to a column of chalcopyrite*, only 4% of the activity came through after 35 free column volumes had been collected (Figure 9). Most of this 4% was collected in the first few free column volumes. It is probable that the initially collected activity was that iodide ion tracer which had gone through the column without reacting with the rock structure.

The results of applying IO_3^- tracer to a chalcopyrite column is shown in Figure 10. In this case 72% of the iodate activity passed through the column in the first three hundred column volumes. Figure 11 shows the results of using IO_3^- tracer on a bournonite** column. Of the applied activity, 47% had passed through the column after 1200 free column volumes†.

These last two columns using IO_3^- tracer were run at a much higher water velocity (10-80 kilometers/year). This water velocity is 20 to 100 times faster than in previous columns and may have caused a non-equilibrium condition. Thus, less tracer would have been absorbed. This explanation of a rate effect (rather than one in which major differences in sorption exist between iodide and iodate ions) was confirmed in batch experiments (discussed below). Furthermore, the deleterious effect of higher water velocities on sorption and the fraction at equilibrium has been demonstrated in a study of the migration of another radionuclide (11). It should be pointed out, however, that the 10-80 kilometer/year velocity is still within the

*Chalcopyrite is a copper iron pyrite mineral, CuFeS_2 .

**Bournonite is a copper sulfide mineral, CuPbSbS_3 .

†The increase around 700 free column volumes is due to a temporary interruption in the water flow and probably was not due to a delayed iodine peak migrating through the column.

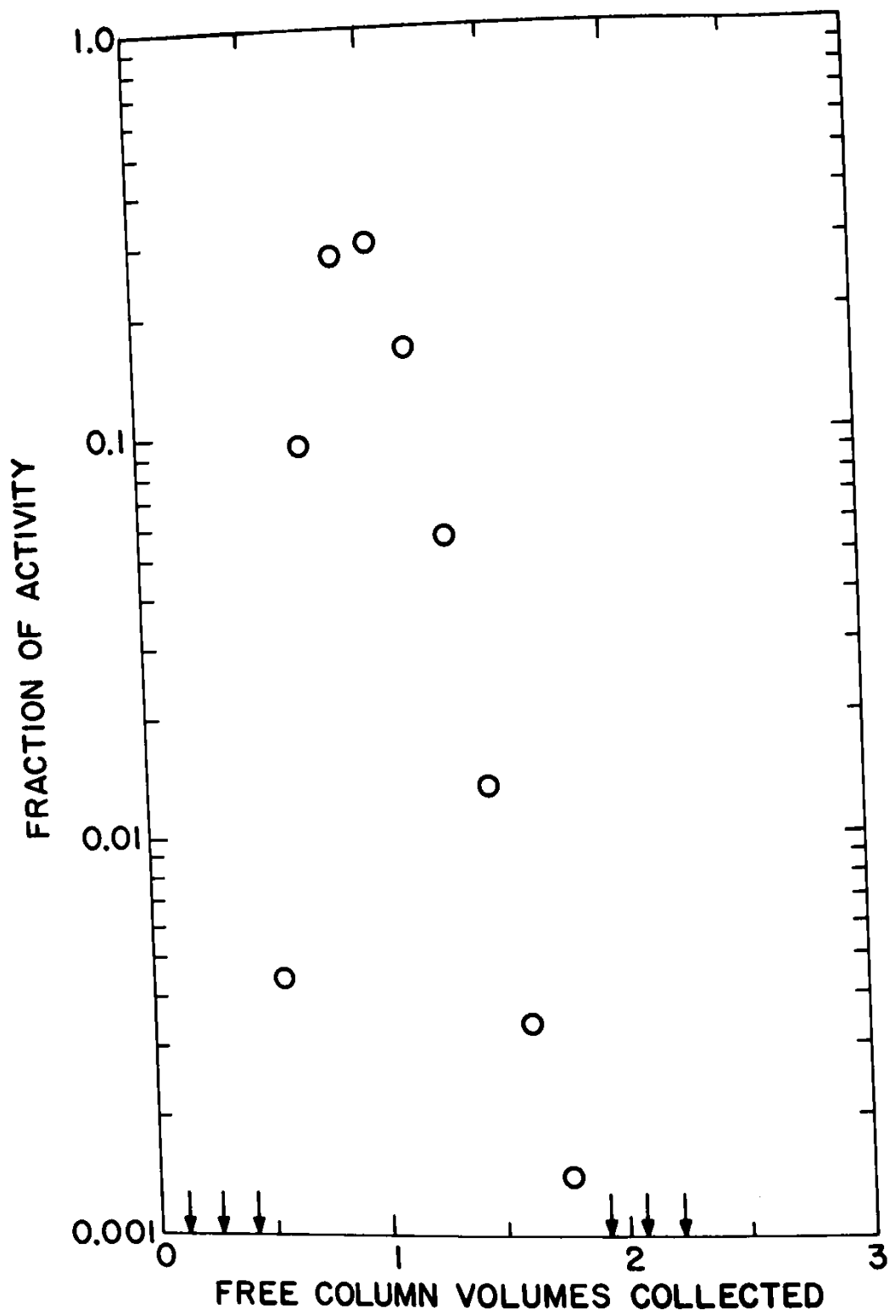


Fig. 7. $^{131}\text{I}^-$ on Saturated Los Alamos Tuff

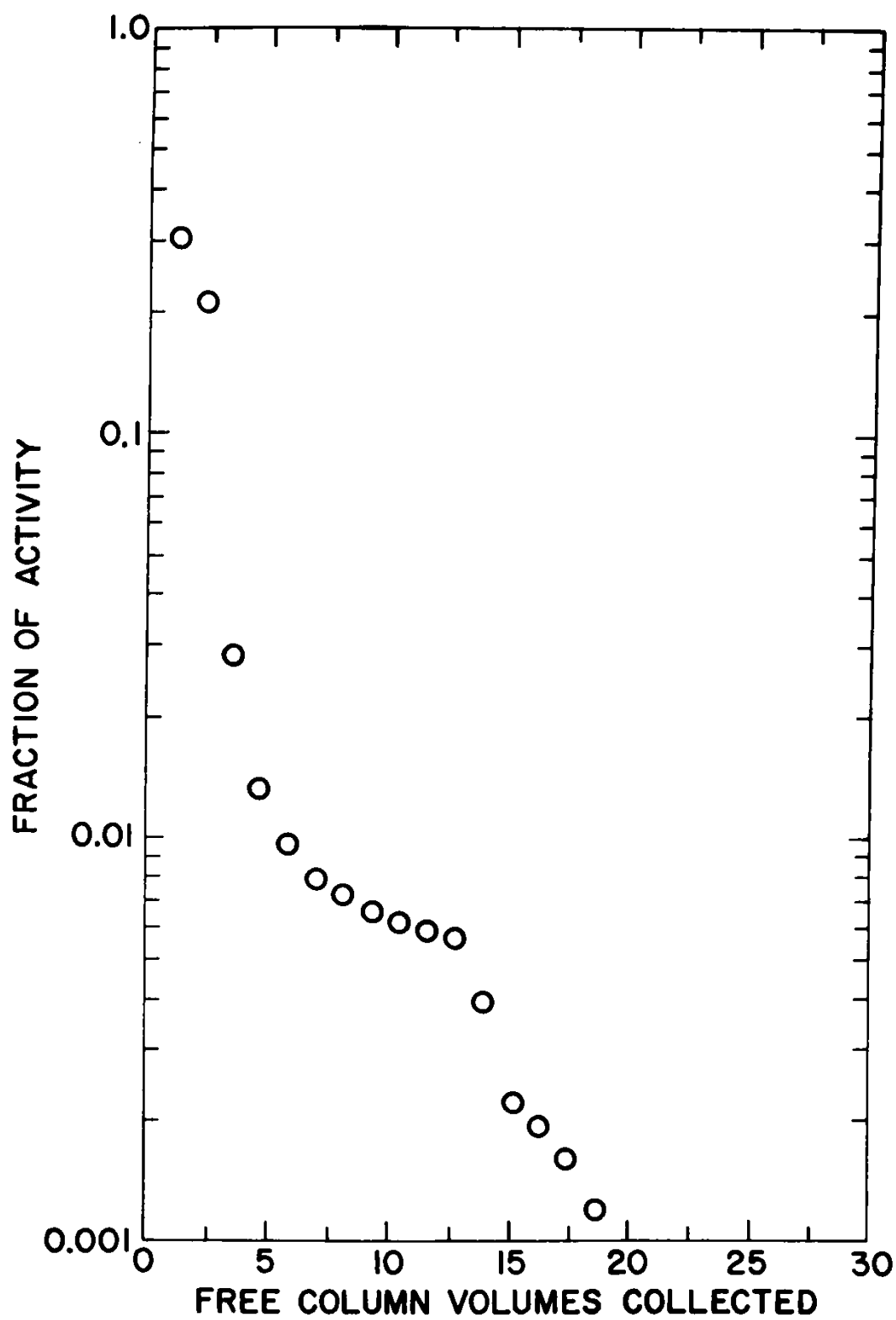


Fig. 8. $^{131}\text{I}^-$ on Limestone

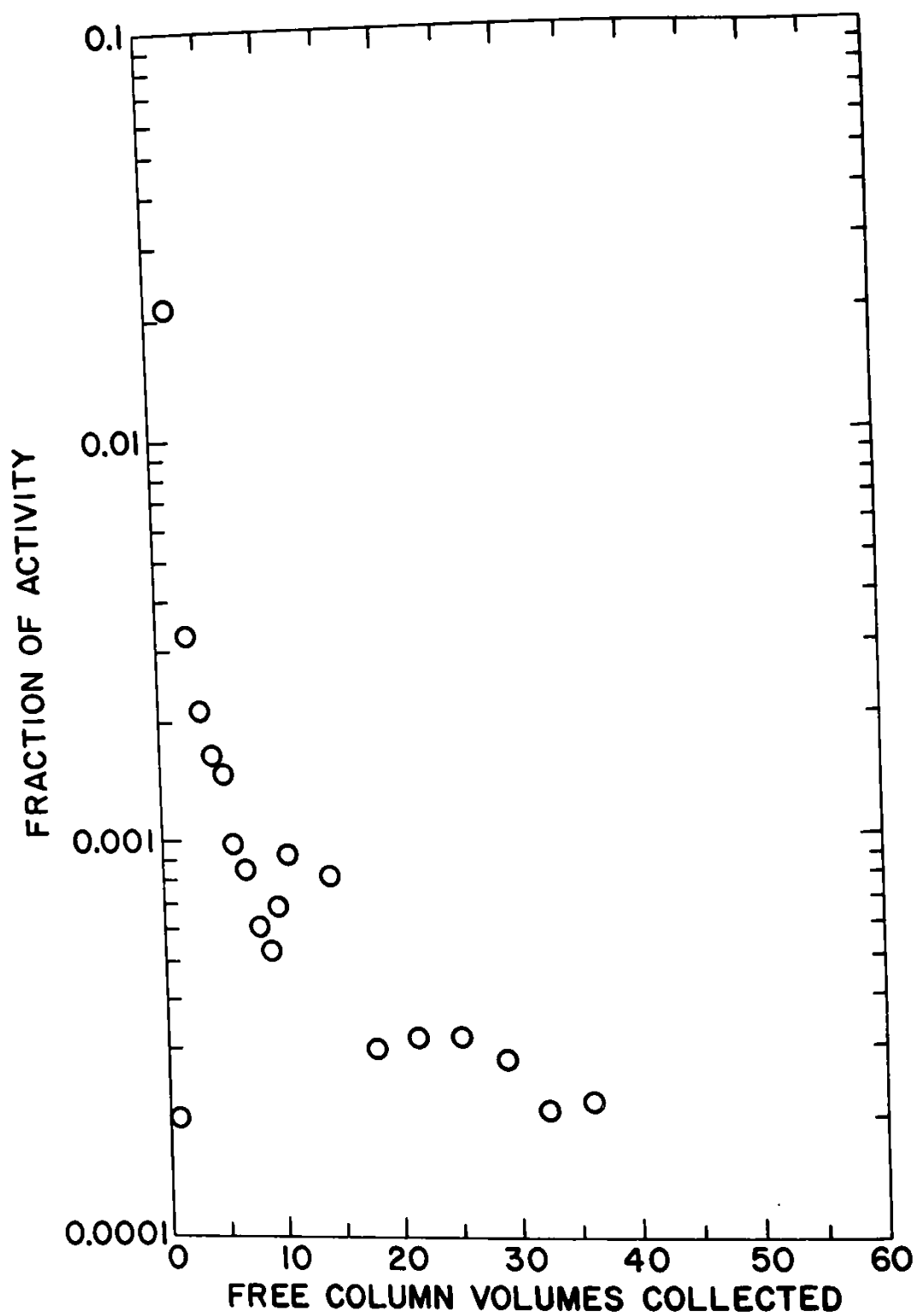


Fig. 9. $^{131}\text{I}^-$ on Chalcopryrite

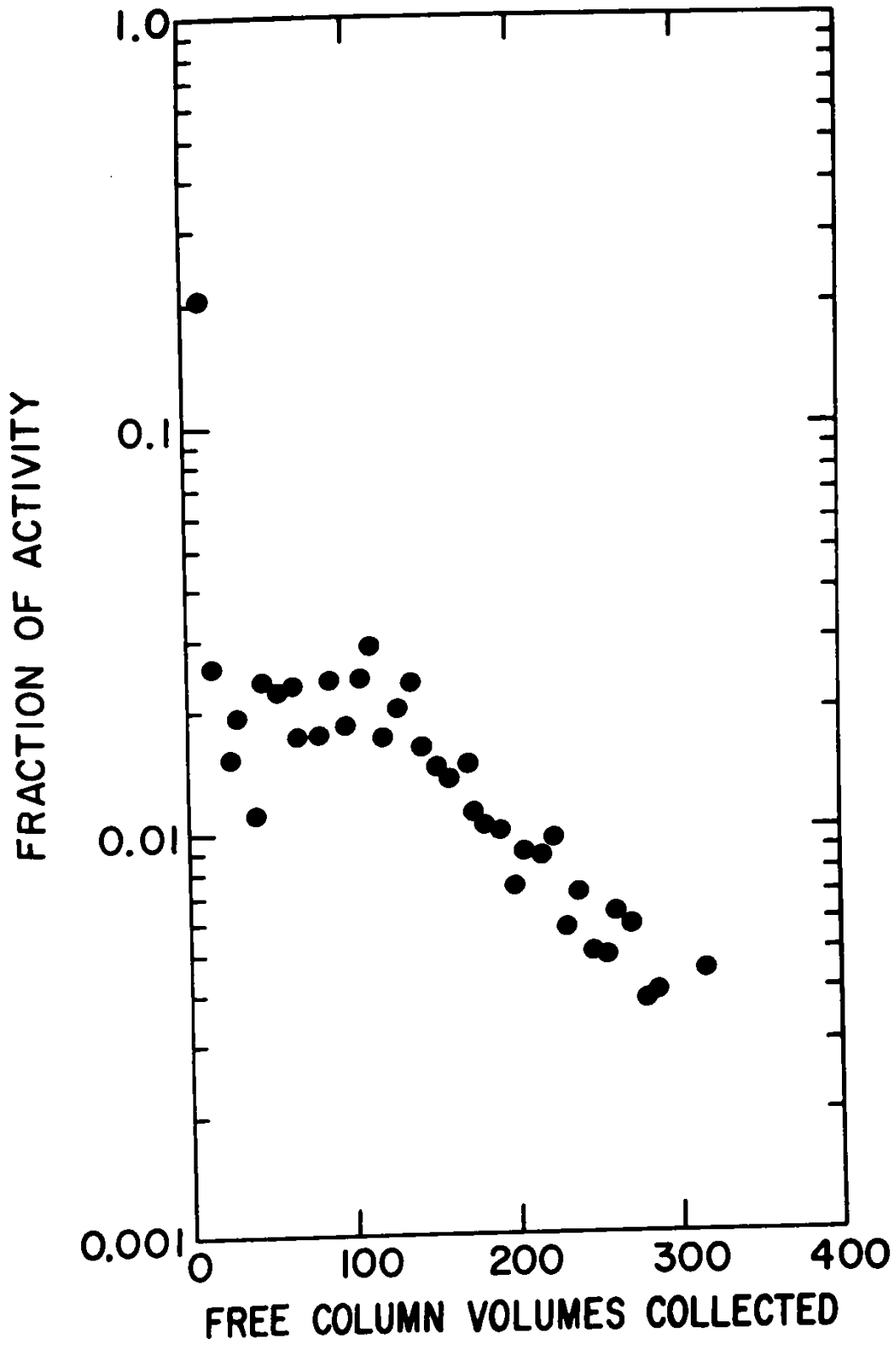


Fig. 10. $^{131}\text{I}-\text{IO}_3^-$ on Chalcopyrite

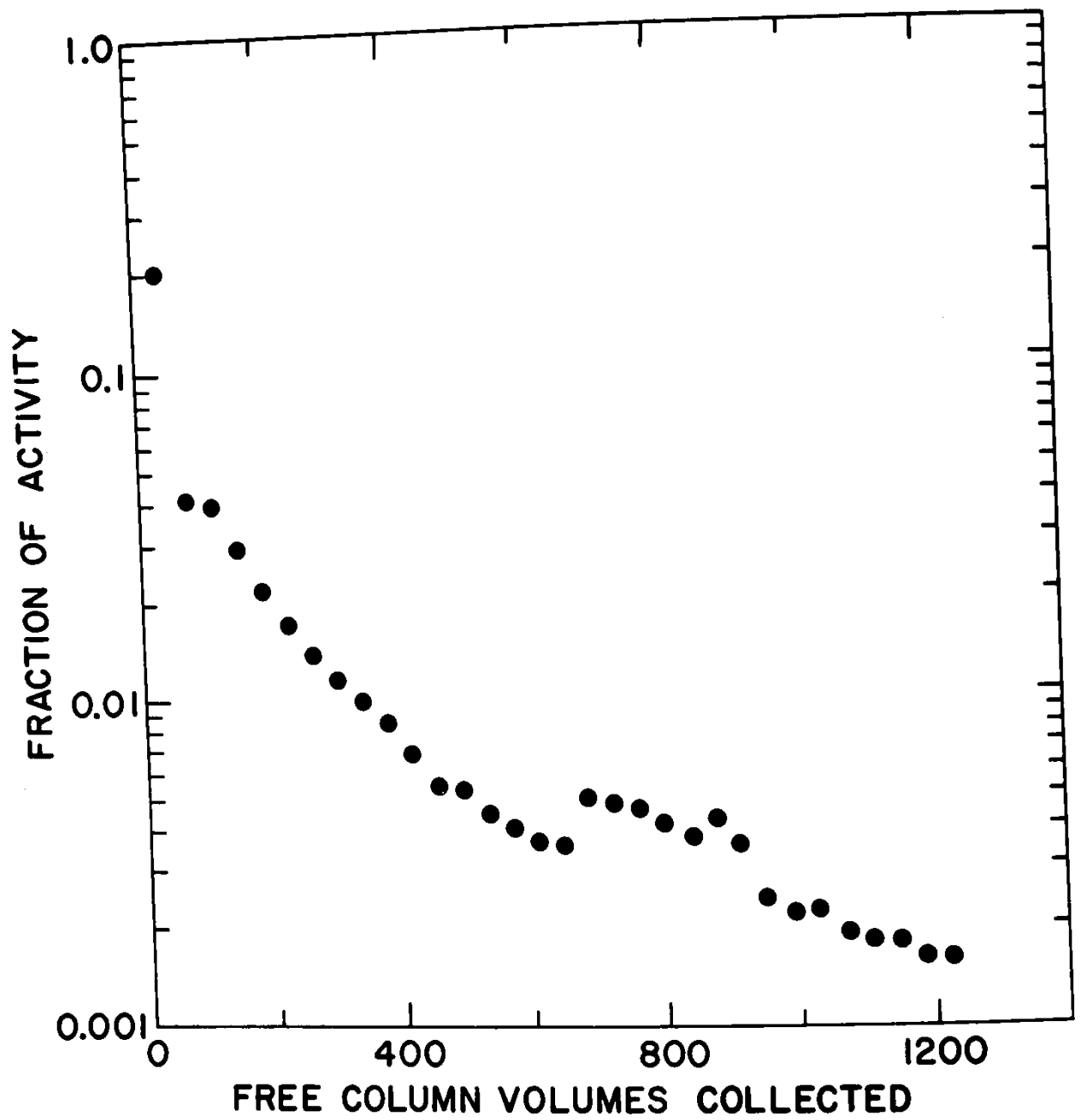


Fig. 11. $^{131}\text{IIO}_3^-$ on Bournonite

extreme upper limit of aquifer flow rates and could conceivably arise if large amounts of water were to inundate a highly fractured rock stratum. Of course, the residence time in the rock stratum would be much longer than in the crushed rock column used in these experiments.

When TcO_4^- tracer was used with a limestone column (Figure 12) 82% of the TcO_4^- tracer came through, mostly within the first two column volumes. When a chalcopyrite column was used, all of the pertechnetate came through (Figure 13). Due to column size, the water velocity was approximately 10 kilometers/year.

The absorption of TcO_4^- on a bournonite column is shown in Figure 14. In this experiment only 10% of the applied activity had come through the column in 250 free column volumes. Again, most of the activity which did elute was found in the first few column volumes. It is felt that this indicates the bulk of the technetium (90%) reacted in some manner with the bournonite and was fixed; the residual (10%) did not have time to react and eluted as TcO_4^- .

C. Batch Experiments

From the data collected from the Biogamma spectrometer and other counting equipment, the fraction of activity sorbed on crushed rock or mineral was determined. The results are shown in Tables V-A and V-B*.

Table V-A. Fraction Sorbed on Crushed Rock^a

Rock or Mineral	TcO_4^-	I^-	IO_3^-
Apatite	0.06	0.19	-
Anhydrite	0.04	-	0.59
Basalt	0.04	0.34	<0.01
Chalk	0.56	0.15	0.59
Dolomite	0.02	0.05	<0.01
Granite	0.16	0.21	0.26
Siltstone	0.04	0.09	0.62
Shale	0.08	0.18	0.36
Los Alamos Tuff	<0.01	0.19	<0.01
NTS Tuff	<0.01	0.23	<0.01

a) In the rocks listed, apatite is a calcium phosphate mineral; anhydrite is calcium sulfate; dolomite is a magnesium-rich limestone; the remainder contain aluminum silicate minerals with varying amounts of other metals such as magnesium, potassium and iron.

Table V-A shows that various silicate rocks as well as other minerals such as apatite ($\text{Ca}(\text{F,Cl})(\text{PO}_4)_3$) and anhydrite (CaSO_4) do not absorb appreciably.

*From batch experiments on vials containing only water or rock-equilibrated solution, it was determined that less than 1% of the TcO_4^- sorbed on the wall of the vial. Approximate 2% or less of the iodide or iodate activity sorbed on the wall. The values listed in the tables, however, do not include these corrections.

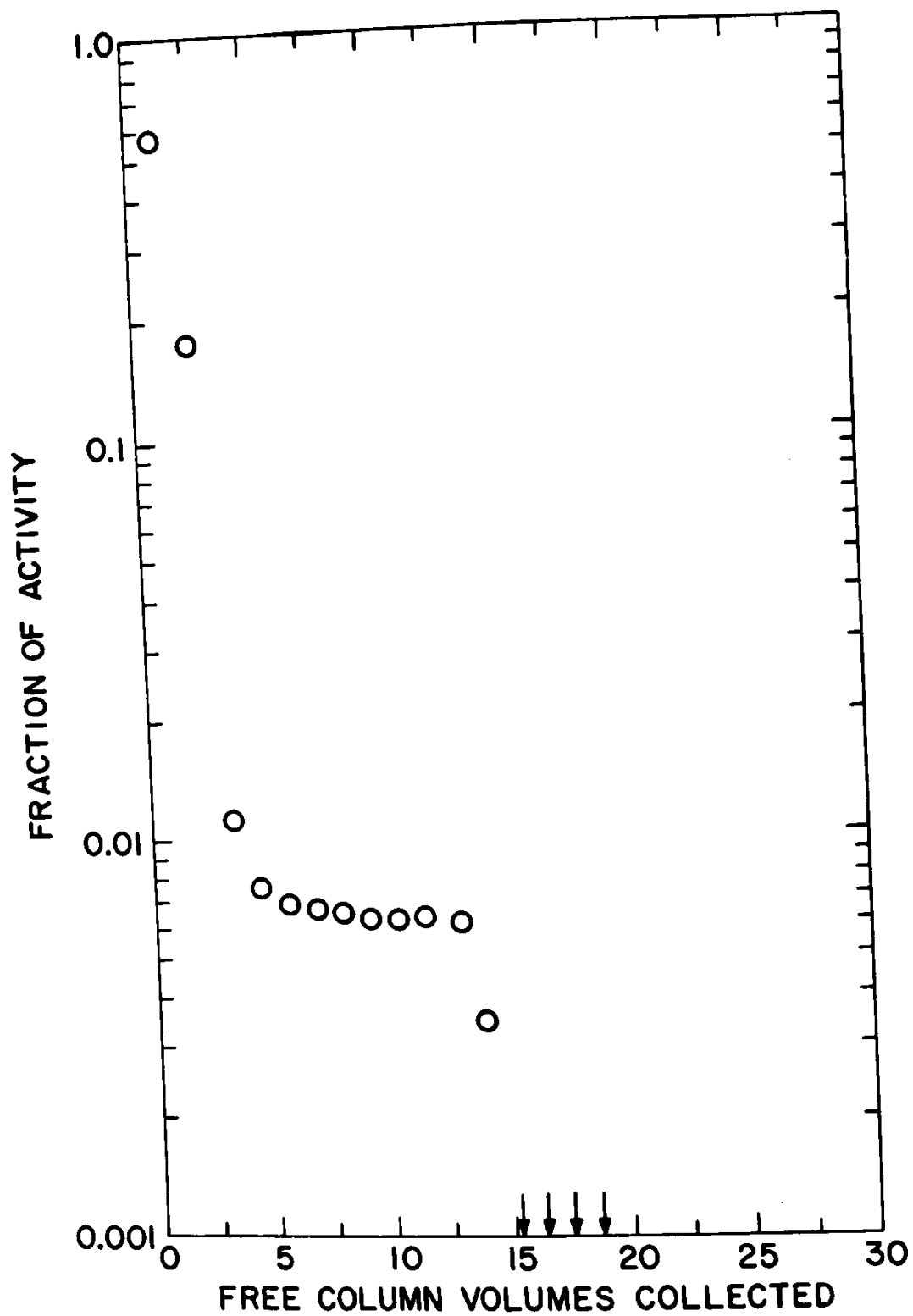


Fig. 12. $^{95m}\text{TcO}_4^-$ on Limestone

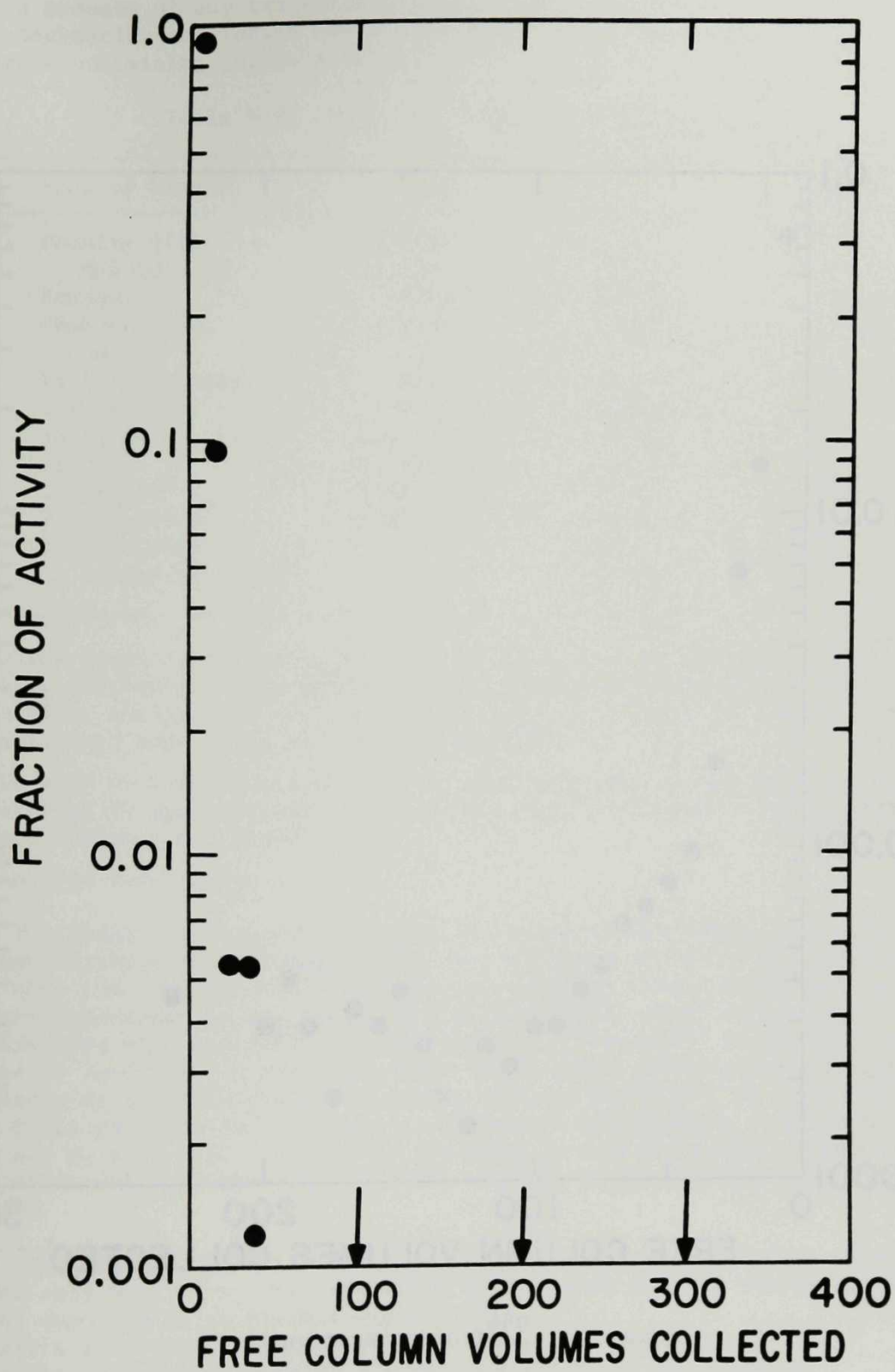


Fig. 13. $^{95m}\text{TcO}_4^-$ on Chalcopryrite

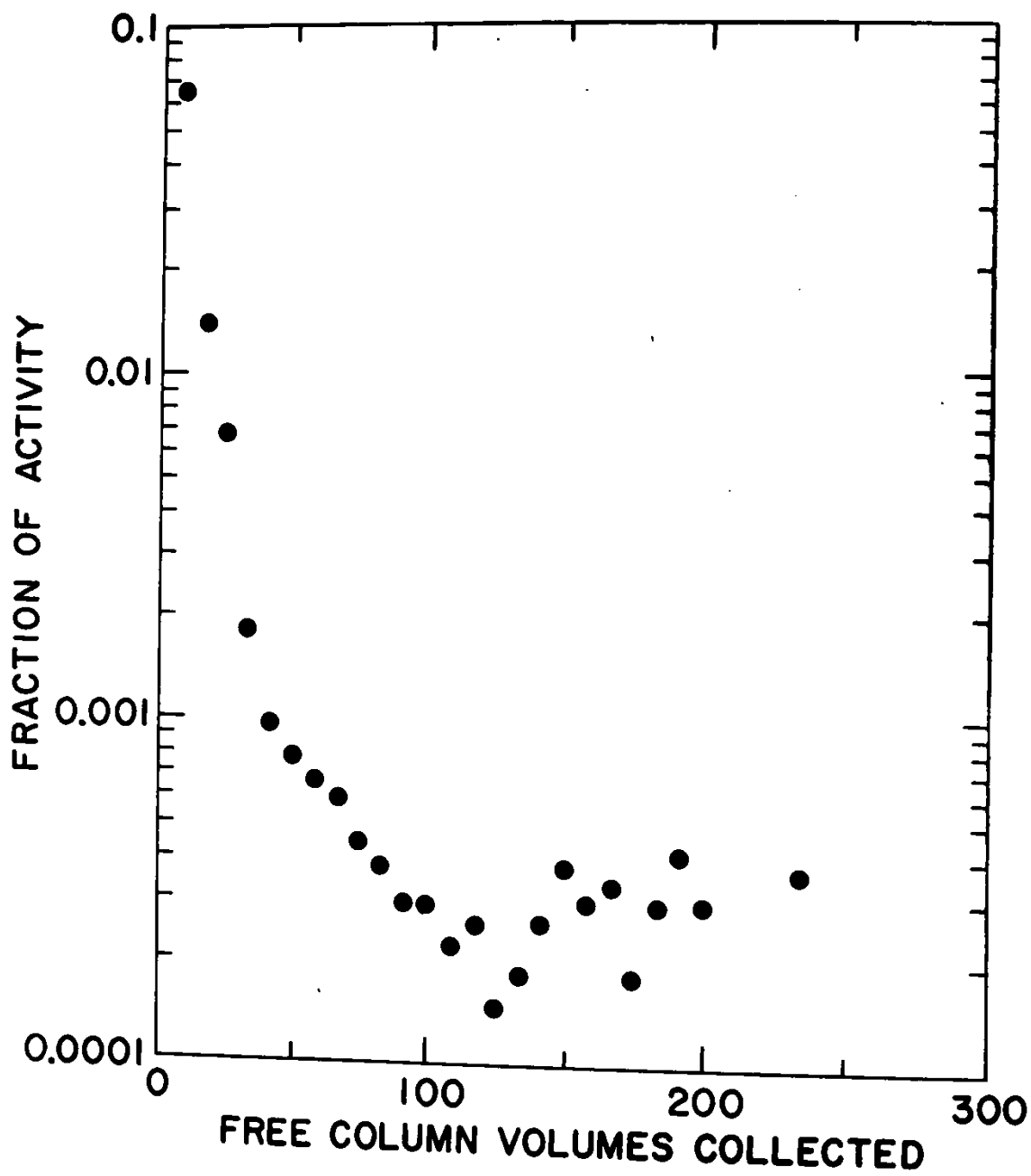


Fig. 14. $^{95m}\text{TcO}_4^-$ on Bournonite

ciable amounts of any tracer used (with a few exceptions*). Table V-B shows that technetium and iodine are absorbed (in some cases almost completely) by minerals containing copper sulfide.

Table V-B. Fraction Sorbed on Crushed Rock^a

Rock or Mineral	TcO_4^-	I^-	IO_3^-
Bornite with Molybdenite	0.22	0.98	0.74
Bournonite	0.98	0.89	0.99+
Chalcopyrite, Canada	0.07	0.99	0.99+
Pyrite, Venezuela	0.54	0.99	0.99+
Chrysocolla	0.76	0.52	0.95
Enargite ^b	0.10-0.81	0.99+	0.97
Galena ^b	0.12, 0.99+	0.87	0.94
Tennantite ^b	0.09, 0.44	0.97	0.86
Tetrahedrite ^b	0.58, 0.99	0.90	0.99+
Tetrahedrite (Argentiferous) ^c	0.85	0.87	0.92

- a) In the minerals listed, pyrite is an iron sulfide, galena is a lead sulfide; molybdenite is a molybdenum sulfide; bournonite is a copper lead sulfide; chrysocolla is a copper silicate; the rest are copper sulfides containing some iron, arsenic, or antimony.
- b) The wide variation in sorption of these minerals is not understood fully, although it appears that it may be related to the mass of the crushed rock used (between 0.2 g and 0.5 g).
- c) Contains some silver.

The results in Table VI are from the batch experiments involving mixed systems in which the solutions were pre-equilibrated with other minerals. They show that the mineral itself rather than the solution seems to be of primary importance in the sorption process. Water which had been pre-equilibrated with minerals such as enargite[†], bornite^{**}, or pyrite^{††} do not appear to increase the sorption capacity of non-sorptive minerals such as siltstone or aluminum oxide. Minerals such as bornite^{***} or azurite^{†††} retain their sorptive ability despite different accompanying solutions. Sorption may be affected, however, by pre-equilibrated solutions of highly soluble minerals, such as salt deposits. Future testing of these solutions is planned.

*The high values for iodate using anhydrite, chalk and siltstone were determined only once. The reasons behind such values are not understood and are being examined in additional experiments.

[†]Enargite is a copper sulfide mineral containing arsenic: Cu_3AsS_4 .

^{**}Bornite is a copper sulfide mineral containing iron: Cu_5FeS_4 .

^{††}Pyrite is an iron sulfide mineral: FeS_2 .

^{***}Bornite is a copper sulfide mineral containing iron: Cu_5FeS_5 .

^{†††}Azurite is a hydrated basic carbonate of copper: $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$.

Table VI
Fraction Sorbed on Mineral

Mineral	Solution	TcO_4^-	I^-
Azurite	Azurite	0.53	0.97
Azurite	Siltstone	0.45	0.94
Bornite	Bornite	0.12	0.97
Bornite	Al_2O_3	0.07	0.98
Enargite	Enargite	0.81	0.99+
Enargite	L.A. Tuff	0.78	0.99+
Enargite	Siltstone	-	0.66
Al_2O_3	Al_2O_3	0.03	-
Al_2O_3	Bornite	0.03	0.04
Al_2O_3	Enargite	<0.01	-
L.A. Tuff	L.A. Tuff	0.02	0.19
L.A. Tuff	Bornite	<0.01	0.17
Siltstone	Siltstone	-	0.12
Siltstone	Enargite	-	0.12
Siltstone	Chalcopyrite, Venezuela	-	0.11

Batch experiments were also carried out using various chemicals in crystalline or powdered form, as shown in Table VII. Cuprous sulfide (Cu_2S) absorbs 99% or more of the pertechnetate, iodide, and iodate activity. However, cupric sulfide (CuS) absorbs only a small fraction (~10%) of the pertechnetate activity. This is an important difference since most of the copper minerals which were shown to absorb technetium and iodine have copper as copper(I). Lead(II) sulfide also appears to absorb technetium as well as the iodine tracers. Other metals (in the sulfides used) exist at their higher oxidation state and so not absorb large amounts of technetium.

Table VII. Fraction Sorbed on Chemical Compounds

Chemical	TcO_4^-	I^-	IO_3^-
Cu_2S	0.99	0.99+	0.99+
CuS	0.05	0.99+	0.99
CdS	0.03	0.97	-
HgS	0.02	0.70	-
PbS	0.60	0.94	0.97
ZnS	0.08	0.10	-
CuO	0.02	0.07	-
PbO_2	<0.01	0.02	-
Fe_2O_3	0.08	0.61	-
CuCl	0.04	0.56	-
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	0.30	0.18	-
FeSO_4	0.65	0.09	-
Ag powder	0.02	0.99+	-

The results of using various oxides and other chemicals are also shown. It is interesting to note that the metal oxides were less effective in the sorption of iodide and were very ineffective in the sorption of technetium.

This could be due to the fact that all of the metal ions were in their higher oxidation state.

It appears that pertechnetate may undergo reduction to a less soluble form or else one more easily incorporated into the lattice structure of the mineral. Ferrous sulfate also appears to absorb technetium. Ferrous sulfate is soluble (16g/100ml H₂O) and the saturated solution used may have introduced problems of recrystallization and entrapment of material from the solution into the crystal. However, little iodide ion was absorbed by ferrous sulfate compared to the sorption of TcO₄⁻. The absorption by ferrous sulfate, pyrite, as well as other ferrous compounds, will be investigated further since it is known that most iron in deep geologic areas exists in reduced form.

Although several of the metal iodides, in the absorbing minerals, are not very soluble, it must be pointed out that iodine is present in concentrations of less than 10⁻¹² molar, well below solubility limits in most cases. However, incorporation into the mineral crystal structure may be the mechanism for the iodine sorption process. At this time, the extent of iodate reduction to iodide is not known.

To investigate the sorptive capacity of the minerals, preliminary experiments were performed using macroscopic amounts of iodide ion. The results in Table VIII show that there is a limit to the ability of the mineral to absorb macroscopic (milligram) amounts of iodide during the three days the mixture was shaken.

Table VIII
Iodide Fraction Sorbed on Minerals

Mineral	Carrier	Tracer
Bornite	0.12	0.97
Chalcopyrite, Germany	0.11	0.98
Tetrahedrite, (Argentiferous)	0.04	0.87
Water*	<0.01	0.02

*The vial contained distilled water and iodide solution with no mineral present. Sorption was on the walls of the vial.

In some of the batch experiments the vials were shaken in an oven at 50-60°C. From a comparison of results of these experiments with the majority of experiments which were done at room temperature, no consistent effect of increased temperature (at least up to 60°C) on the absorption of iodine and technetium has been observed. Additional experiments to better measure even small effects of temperature change are planned.

SUMMARY AND CONCLUSIONS

The objective of these experiments was to investigate the absorption of iodine and technetium anions by various common minerals. Two basic techniques were employed to study the absorption of radiotracers: (a) column elution using rock cores or crushed rock columns, and (b) batch sorption experiments using crushed rock or minerals.

From the work performed several conclusions may be drawn:

1. Up to 99+% of technetium and iodine tracers ($<10^{-10}$ M) can be absorbed by a variety of minerals (in less than gram quantities) through mechanisms other than ion-exchange. In mineral columns having high absorption, an initial small peak within the first few free column volumes was the only major contribution to activity eluting from the rock column and was probably due to unreacted tracer. Despite a range of absorption values for different minerals containing copper sulfide, no delayed migration peak, typical of an ion-exchange process, was observed; this may be due to an insufficient elution volume. However, in mineral columns with less observed absorption, there was also no delayed migration peak present even though these were sufficiently eluted.
2. There is evidence that oxidation-reduction may be involved with the sorption of the pertechnetate anion. This appears to be the case for minerals containing cuprous ions (or plumbous and ferrous ions). Sulfide compounds containing metal ions in the highest oxidation state were not effective in the sorption of pertechnetate tracer. Oxide compounds containing copper, lead, or iron in the highest oxidation state also absorb little technetium.
3. In the sorption of iodide ions, coprecipitation or incorporation into a crystal lattice may be the mechanism involved. This is indicated by the high degree of absorption in minerals and chemicals containing metal ions that form metal iodides of low solubility.
4. The absorption of iodate ions appears to coincide with iodide ion absorption, although it cannot be said at this time whether the mechanism is the same. There is a possibility of iodate reduction to either iodine or iodide.
5. The mechanisms for large absorption of both technetium and iodine, in the minerals examined, are related to the mineral surface or structure itself, rather than to dissolved or colloidal material present in rock-equilibrated solutions. This would preclude a simple precipitation-filtration mechanism especially at tracer concentrations. Such a relationship to the mineral structure is important since it is not likely that the chemical composition of groundwater will remain constant as it passes through various mineral areas.
6. The rate of absorption is apparently slow enough so that equilibrium is not reached under high water front velocities of ~ 10 -80 kilometers/year. Whether and how much temperature and total mineral surface area also affect anionic sorption are details which must be studied further.
7. The ability of the sulfide minerals to absorb iodine (and presumably technetium) is limited. From the carrier absorption experiment, an estimated absorption capability for chalcopyrite would be ~ 300 micrograms/gram of crushed chalcopyrite. This, however, is probably an upper limit for chalcopyrite in a rock stratum.

More information on the exact mechanisms and reaction rates for the sorption of technetium and iodine is needed, especially under conditions which may approximate those found in deep geologic strata. Such research

would be helpful not only for technetium and iodine, but also for other radioactive wastes which may form anionic species in groundwater solutions. In addition, the importance of distinguishing between various chemical oxidation states of these elements, especially at different pH and Eh values, has been recognized, and work is presently going forward to identify specific chemical oxidation states at tracer concentrations.

DISCUSSION

Consideration of the foregoing experimental results as well as discussion with other groups interested in migration leads to conclusions which may strongly influence the direction and the details of future efforts.

There appears to be a more or less general agreement among the laboratory modeling results, the field coring results and analysis of the LASL site. It suggests that so far the laboratory modeling technique may have some empirical validity in evaluating migration in a real repository.

The absorption of binding of radionuclides in lithic materials and the consequent retardation of migration from a repository appears to be strongly dependent on the sign and magnitude of the formal charge on the ions as well as the solubility of the particular compounds or reaction product with rocks or minerals. The negatively charged ions such as I^- , IO_3^- , and TcO_4^- are bound only slightly to the type of rocks which strongly bind the positive ions Am(III), Pu(IV) and Np(V). The immobilization of the first set (negative ions) seems to depend primarily on their reaction to form insoluble compounds with certain minerals containing copper, lead and sulfur. It is known that Tc_2S_7 is very insoluble and co-precipitates with copper sulfide and that lead and cuprous copper form insoluble iodides. All of the foregoing, of course, were self-evident but nevertheless the experiments had to be performed and the data collated. To make facile assumptions regarding the reactions of heterogeneous natural materials with tracer scale radionuclides invites error and the possibility of overlooking subtle effects.

The possibility now exists that the normally labile anions may be "gettered" by surrounding the originally emplaced canister with a packing of the appropriate minerals; chalcopyrite, galena, etc., if these are not already present in the enveloping rock strata.

It also appears that certain common mineral components of rocks, notably those containing Fe(II) are capable of reducing some actinides in neutral solution to lower oxidation states. Examples are: Np(V) is reduced to Np(IV) and Pu(IV) to Pu(III). These reductions may have a profound long-term effect on the migration of certain actinides.

The qualification mentioned in the preceding paragraph is pointed out because so far these reactions have only been observed between "macro amounts" of Pu and Np (micrograms per ml.) and Fe(II) in solution (milligrams per ml.). It should be pointed out that such large amounts of reactants were employed in the interest of both speeding up the reactions and being able to observe the reductions spectrophotometrically. Naturally with trace amounts of actinides and trace amounts of Fe(II) the reaction would tend to be much slower, and the difficulty of determining the extent of reaction would be vastly increased.

It is, of course, intended to carry these reactions out on a tracer level with the amounts of Fe(II) yielded naturally (at pH \sim 7) from known minerals such as fayalite, siderite, magnetite, etc. It is expected, however, that these reactions will require substantial periods of time to complete.

As a result of consultations with individuals at Chalk River Nuclear Laboratory (CRNL) and at Idaho National Engineering Laboratory (INEL) we have agreed to undertake the analysis of core samples and hope to arrive at a set of determinations similar to that carried out with LASL. These data obtained using quite different material than the Los Alamos tuff previously studied will possibly enable us to generalize and extend the usefulness of

the laboratory model more than is proper with the limited data presently available.

Further consultation with other groups (Sandia and the U.S. Geological Survey at INEL) has focused attention on the likelihood that radionuclide bearing groundwater frequently moves through fissures in rocks. Generally these fissures are filled with clays in which case the migration characteristic of a given radionuclide is that determined in part by the clay rather than the matrix rock.

Some cores from INEL basalt have been generously supplied to us by the USGS. These cores were chosen by them (at our request) so that they embodied naturally occurring fissures. If these cores can be manipulated so the fissures are not mechanically disturbed, attempts will be made to observe the migration characteristics of radionuclides through a real fissure.

In addition, it has become apparent that the movement of radionuclides in salt at the Waste Isolation Pilot Plant (WIPP) may also be in fissures in the polycrystalline WIPP salt. It appeared useful to initiate some kind of cooperative program with Sandia on migration through salt.

An informal cooperative program with Sandia Laboratories initiating a study of this nature has been undertaken. The particular techniques and tracers (^{239}Np , ^{235}Np , ^{237}U , ^{237}Pu and ^{241}Am) used in previous work will be employed.

The salt experiments will have to be performed in saturated brine solutions. Since temperature fluctuations of even 0.01°C can result in the dissolution or precipitation of hundreds of atomic layers of NaCl on the surface of the fissures, these in turn can release or entrap large amounts of activity. This possible dependency on temperature imposes great experimental difficulties which have not yet been resolved. Nevertheless it is believed to be important to undertake the migration experiments since the only firm proposal for a geologic stratum for waste isolation is in salt.

It may be apropos in this discussion to make a statement about our laboratory procedures. We are well aware that there is some pressure to provide chemical analysis of the mineral content of the water used in the experiments described in this report. The water used is invariably pre-equilibrated with the particular material undergoing testing unless there is some reason for variation. This is accomplished by contacting the granulated rock with de-ionized water for weeks or months. The pH is also determined.

It would be easy (though expensive and time consuming) to determine and list the silica, sodium, fluoride, etc., of every sample of water corresponding to each sample of rock. What is not clear, however, is whether any added pertinent knowledge is to be obtained from this collection of numbers. Regardless of whether the formal analyses of the water solution of the rock is known, the composition of water in a real aquifer will be determined by the mineral composition of the strata through which it passes and the analysis is irrelevant.

To give the analytical data as part of the experimental description implies that these are parameters which somehow can be manipulated or used to predict the migratory behavior of radionuclides in an aquifer. This is illusory and misleading and obfuscates the issue, which really is; what are the migration properties of given radionuclides in a real geological stratum mobilized by real water in passing through its particular environment. The actual analysis of the mineral content of a given sample of water in a laboratory model is largely irrelevant so long as the water is equilibrated as closely as possible with the rock under consideration. The true site eval-

uation should be carried out on rock from the chosen site with water from a designated aquifer under the conditions and flow rate and temperature that exist.

Thus it has not been deemed necessary or even advisable to carry out these analyses. However, if it can be shown that such analyses will contribute within the next two years or so to the choice and evaluation of a repository then these data will be well worth the trouble.

There is no doubt that the exact composition of the aqueous phase will affect the binding of radionuclides to rocks (as will the exact composition of the rock itself). A true basic study of the absorption coefficients will have to establish these parameters and this should be investigated in a program of basic research.

However, geological strata are heterogeneous mixtures of many mineral types and since the aim of this program is to obtain data applicable to migration in real strata within a short time frame, we are primarily concerned with parameters averaged over the various mineralogical components. The comparison of the laboratory model of the Los Alamos disposal site with the migration behavior of Am and Pu at the real site appears to suggest that this approach may be practical.

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